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(54) **MARTENSITIC STAINLESS STEEL MATERIAL**

(57) A martensitic stainless steel material having high strength, and having excellent corrosion resistance in a corrosive environment in which SO_x or NO_x is mixed is provided. The martensitic stainless steel material according to the present disclosure satisfies a chemical composition described herein, and satisfies Formula (1). The yield strength is 862 MPa or more. In the martensitic stainless steel material, a number ratio of Mg oxides having an equivalent circular diameter of 2.0 μm or more with respect to Ca oxides having an equivalent circular diameter of 2.0 μm or more, Ca sulfides having

an equivalent circular diameter of 2.0 μm or more, and the Mg oxides having an equivalent circular diameter of 2.0 μm or more is 45.0% or more.

$$0.0010 \leq \text{Ca} + \text{Mg} \leq 0.0050 \dots (1)$$

Where, a content of a corresponding element in percent by mass is substituted for each symbol of an element in Formula (1).

Description

TECHNICAL FIELD

- 5 **[0001]** The present disclosure relates to a steel material, and more particularly relates to a martensitic stainless steel material.

BACKGROUND ART

- 10 **[0002]** An increase in the concentration of carbon dioxide (CO₂) above ground is currently a global problem. Therefore, efforts to suppress CO₂ emissions are proceeding. One such effort to suppress CO₂ emissions that is attracting particular attention is CCUS.

- [0003]** CCUS is an abbreviation for "carbon dioxide capture, utilization and storage". That is, CCUS includes the three technologies of capturing, utilizing, and storing CO₂. Among these, as technology for storing CO₂, technology which captures CO₂ emitted from an industrial facility such as an electric power plant or a factory, and injects the CO₂ into a depleted oil well to store the CO₂ therein is attracting attention.

- [0004]** A steel material to be used for such kind of CO₂ storage technology is required to have high strength in order to inject CO₂ into a depleted oil well. Further, CO₂ is a corrosive substance that corrodes the steel material. Therefore, a steel material to be used for CO₂ storage technology is required to have excellent corrosion resistance in a corrosive environment that contains a large amount of CO₂.

- [0005]** Martensitic stainless steel materials containing about 13% by mass of Cr that are typified by API L80 13Cr steel material and Super 13Cr steel material in which the content of C is reduced are already known as steel materials which have high strength and which are excellent in corrosion resistance in corrosive environments. Specifically, Japanese Patent Application Publication No. 2000-192196 (Patent Literature 1), and Japanese Patent Application Publication No. 2012-136742 (Patent Literature 2) each propose a martensitic stainless steel material which has high strength and which is excellent in corrosion resistance in a corrosive environment.

- [0006]** The martensitic stainless steel material proposed in Patent Literature 1 is a martensitic stainless steel for oil wells consisting of, in weight%, C: 0.001 to 0.05%, Si: 0.05 to 1%, Mn: 0.05 to 2%, P: 0.025% or less, S: 0.01% or less, Cr: 9 to 14%, Mo: 3.1 to 7%, Ni: 1 to 8%, Co: 0.5 to 7%, sol. Al: 0.001 to 0.1%, N: 0.05% or less, O (oxygen): 0.01% or less, Cu: 0 to 5%, and W: 0 to 5%, with the balance being Fe and impurities. When a steel material contains Mo, the Ms point decreases. Therefore, because this steel material contains Co as well as Mo, a decrease in the Ms point is suppressed, and the microstructure is made a martensitic single-phase structure. It is disclosed in Patent Literature 1 that, as a result, in this steel material, the corrosion resistance in a corrosive environment can be increased while maintaining the strength at a yield strength of 551 MPa or more.

- [0007]** The martensitic stainless steel material proposed in Patent Literature 2 is a martensitic stainless steel seamless pipe consisting of, in mass%, C: 0.01% or less, Si: 0.5% or less, Mn: 0.1 to 2.0%, P: 0.03% or less, S: 0.005% or less, Cr: 14.0 to 15.5%, Ni: 5.5 to 7.0%, Mo: 2.0 to 3.5%, Cu: 0.3 to 3.5%, V: 0.20% or less, Al: 0.05% or less, and N: 0.06% or less, with the balance being Fe and impurities. This steel material has a yield strength of 655 to 862 MPa, and a yield ratio of 0.90 or more. It is disclosed in Patent Literature 2 that with respect to this steel material, by making the content of C 0.01% or less, adjusting Cr, Ni and Mo to within a preferable range, and also containing suitable amounts of Cu and V or a suitable amount of W, excellent corrosion resistance is obtained in a corrosive environment.

CITATION LIST

45 PATENT LITERATURE

[0008]

- Patent Literature 1: Japanese Patent Application Publication No. 2000-192196
50 Patent Literature 2: Japanese Patent Application Publication No. 2012-136742

SUMMARY OF INVENTION

TECHNICAL PROBLEM

- 55 **[0009]** As mentioned above, according to the technology for storing carbon dioxide (CO₂), captured CO₂ is injected into a depleted oil well or the like and stored therein. On the other hand, in some cases oxides such as SO_x or NO_x are mixed in CO₂ that is captured from an industrial facility such as an electric power plant or a factory. The term "SO_x" is a generic term

for sulfur oxides typified by SO₂. The term "NOx" is a generic term for nitrogen oxides typified by NO₂. SOx or NOx dissolves in water and forms an acidic compound (sulfates, nitrates and the like). That is, when SOx or NOx is mixed in CO₂, the corrosive environment tends to become acidic, and the steel material in the corrosive environment is liable to be further corroded. Therefore, a steel material to be used for such kind of carbon dioxide storage technology is required to have not only high strength, but also to have excellent corrosion resistance in a corrosive environment in which SOx or NOx is mixed.

[0010] The aforementioned Patent Literatures 1 and 2 propose martensitic stainless steel materials that have high strength and excellent corrosion resistance in a corrosive environment. However, in the aforementioned Patent Literatures 1 and 2, the corrosion resistance of the steel material in a corrosive environment in which SOx or NOx is mixed has not been examined at all.

[0011] An objective of the present disclosure is to provide a martensitic stainless steel material that has high strength, and has excellent corrosion resistance in a corrosive environment in which SOx or NOx is mixed.

SOLUTION TO PROBLEM

[0012] A martensitic stainless steel material according to the present disclosure consists of, in mass%,

C: 0.030% or less,
 Si: 1.00% or less,
 Mn: 1.00% or less,
 P: 0.030% or less,
 S: 0.0050% or less,
 Cr: 11.00 to 14.00%,
 Ni: 4.00 to 7.50%,
 Mo: 1.50 to 4.50%,
 Co: 0.01 to 0.50%,
 Ti: 0.05 to 0.30%,
 V: 0.01 to 1.00%,
 Ca: 0.0005 to 0.0050%,
 Mg: 0.0005 to 0.0050%,
 Al: 0.001 to 0.100%,
 N: 0.0500% or less,
 O: 0.0500% or less,
 Cu: 0 to 3.50%,
 Nb: 0 to 0.50%,
 Zr: 0 to 0.050%,
 W: 0 to 2.00%,
 B: 0 to 0.0050%,
 rare earth metal: 0 to 0.0050%, and
 the balance: Fe and impurities,
 wherein:

within ranges of contents of elements of the martensitic stainless steel material, contents of the elements satisfy Formula (1);

a yield strength is 862 MPa or more; and
 in the martensitic stainless steel material,

a number ratio of Mg oxides having an equivalent circular diameter of 2.0 μm or more with respect to Ca oxides having an equivalent circular diameter of 2.0 μm or more, Ca sulfides having an equivalent circular diameter of 2.0 μm or more, and the Mg oxides having an equivalent circular diameter of 2.0 μm or more is 45.0% or more;

$$0.0010 \leq \text{Ca} + \text{Mg} \leq 0.0050 \dots (1)$$

where, a content of a corresponding element in percent by mass is substituted for each symbol of an element in Formula (1).

ADVANTAGEOUS EFFECTS OF INVENTION

[0013] The martensitic stainless steel material according to the present disclosure has high strength and has excellent corrosion resistance in a corrosive environment in which SO_x or NO_x is mixed.

DESCRIPTION OF EMBODIMENTS

[0014] First, the present inventors conducted studies from the viewpoint of the chemical composition with respect to a martensitic stainless steel material that has high strength and has excellent corrosion resistance in a corrosive environment in which SO_x or NO_x is mixed. As a result, the present inventors considered that if a martensitic stainless steel material consists of, in mass%, C: 0.030% or less, Si: 1.00% or less, Mn: 1.00% or less, P: 0.030% or less, S: 0.0050% or less, Cr: 11.00 to 14.00%, Ni: 4.00 to 7.50%, Mo: 1.50 to 4.50%, Co: 0.01 to 0.50%, Ti: 0.05 to 0.30%, V: 0.01 to 1.00%, Ca: 0.0005 to 0.0050%, Mg: 0.0005 to 0.0050%, Al: 0.001 to 0.100%, N: 0.0500% or less, O: 0.0500% or less, Cu: 0 to 3.50%, Nb: 0 to 0.50%, Zr: 0 to 0.050%, W: 0 to 2.00%, B: 0 to 0.0050%, rare earth metal: 0 to 0.0050%, and the balance: Fe and impurities, there is a possibility that both a yield strength of 862 MPa (125 ksi) or more and excellent corrosion resistance in a corrosive environment in which SO_x or NO_x is mixed can be obtained.

[0015] Here, in a martensitic stainless steel material that has the aforementioned chemical composition and has a yield strength of 862 MPa or more, in some cases oxygen (O) in the steel material is immobilized as a Ca oxide by Ca, and the O solubility in the steel material decreases. In this case, Ca oxides are formed in the steel material. On the other hand, as a result of detailed studies conducted by the present inventors, it has been revealed that in a corrosive environment in which SO_x or NO_x is mixed, coarse Ca oxides are liable to become a starting point of pitting. Here, as mentioned above, when SO_x or NO_x is mixed therein, a corrosive environment tends to become acidic, and the pH in the environment decreases. On the other hand, Ca oxides easily dissolve in an acidic environment. Therefore, in a corrosive environment in which SO_x or NO_x is mixed and the pH has decreased, there is a possibility that coarse Ca oxides will dissolve and become a starting point of pitting. That is, it has been revealed by the studies of the present inventors that when a large number of coarse Ca oxides are formed in a steel material, there is a possibility that excellent corrosion resistance will not be obtained in a corrosive environment in which SO_x or NO_x is mixed.

[0016] Therefore, the present inventors conceived of immobilizing O as an Mg oxide with Mg instead of Ca to increase the corrosion resistance of the steel material. In comparison to Ca oxides, Mg oxides are difficult to dissolve even under an acidic environment. Therefore, if Mg oxides are formed in the steel material instead of Ca oxides, there is a possibility that the corrosion resistance of the steel material in a corrosive environment in which SO_x or NO_x is mixed can be increased.

[0017] Here, in the present description, Ca oxides having an equivalent circular diameter of 2.0 μm or more are also referred to as "coarse Ca oxides". Further, in the present description, Ca sulfides having an equivalent circular diameter of 2.0 μm or more are also referred to as "coarse Ca sulfides". In addition, in the present description, Mg oxides having an equivalent circular diameter of 2.0 μm or more are also referred to as "coarse Mg oxides". Furthermore, in the present description, coarse Ca oxides, coarse Ca sulfides, and coarse Mg oxides are also collectively referred to as "specific inclusions". The specific inclusions are inclusions which, in a martensitic stainless steel material having the aforementioned chemical composition, are obtained as a result of O or S being immobilized as an oxide or a sulfide by Ca or Mg.

[0018] As a result of detailed studies conducted by the present inventors it has been revealed that if the number ratio of coarse Mg oxides with respect to coarse Ca oxides, coarse Ca sulfides, and coarse Mg oxides is 45.0% or more, in a martensitic stainless steel material having the aforementioned chemical composition, both a yield strength of 862 MPa or more and excellent corrosion resistance in a corrosive environment in which SO_x or NO_x is mixed can be obtained. That is, the martensitic stainless steel material according to the present embodiment has the aforementioned chemical composition, and the number ratio of coarse Mg oxides with respect to the specific inclusions in the martensitic stainless steel material is made 45.0% or more. As a result, the martensitic stainless steel material according to the present embodiment has a yield strength of 862 MPa or more, and excellent corrosion resistance in a corrosive environment in which SO_x or NO_x is mixed.

[0019] As a result of further detailed studies conducted by the present inventors based on the above findings, it has been revealed that in addition to having the aforementioned chemical composition, by the chemical composition satisfying Formula (1), the number ratio of coarse Mg oxides with respect to the specific inclusions is stably increased to 45.0% or more.

$$0.0010 \leq \text{Ca} + \text{Mg} \leq 0.0050 \dots (1)$$

[0020] Where, a content of a corresponding element in percent by mass is substituted for each symbol of an element in Formula (1).

[0021] Let Fn1 be defined as $\text{Fn1} = \text{Ca} + \text{Mg}$. Fn1 is an index that relates to Ca oxides and Mg oxides. If Fn1 is too low, Ca

and Mg cannot sufficiently immobilize O as an oxide, and O remains in the steel material in a partially dissolved state. On the other hand, if Fn1 is too high, in some cases Mg oxides may be modified by Ca, and the number ratio of coarse Mg oxides with respect to the specific inclusions will decrease. Accordingly, in the present embodiment, on the premise of having the aforementioned chemical composition, Fn1 is to be within the range of 0.0010 to 0.0050.

[0022] As described above, in addition to having the aforementioned chemical composition, the martensitic stainless steel material according to the present embodiment satisfies Formula (1), also has a yield strength of 862 MPa or more, and in addition, the number ratio of coarse Mg oxides with respect to the specific inclusions is made 45.0% or more. As a result, the martensitic stainless steel material according to the present embodiment has high strength and has excellent corrosion resistance in a corrosive environment in which SOx or NOx is mixed.

[0023] The gist of the martensitic stainless steel material according to the present embodiment, which has been completed based on the above findings, is as follows.

[0024]

[1] A martensitic stainless steel material consisting of, in mass%,

C: 0.030% or less,
Si: 1.00% or less,
Mn: 1.00% or less,
P: 0.030% or less,
S: 0.0050% or less,
Cr: 11.00 to 14.00%,
Ni: 4.00 to 7.50%,
Mo: 1.50 to 4.50%,
Co: 0.01 to 0.50%,
Ti: 0.05 to 0.30%,
V: 0.01 to 1.00%,
Ca: 0.0005 to 0.0050%,
Mg: 0.0005 to 0.0050%,
Al: 0.001 to 0.100%,
N: 0.0500% or less,
O: 0.0500% or less,
Cu: 0 to 3.50%,
Nb: 0 to 0.50%,
Zr: 0 to 0.050%,
W: 0 to 2.00%,
B: 0 to 0.0050%,
rare earth metal: 0 to 0.0050%, and
the balance: Fe and impurities,
wherein:

within ranges of contents of elements of the martensitic stainless steel material, contents of the elements satisfy Formula (1);
a yield strength is 862 MPa or more; and
in the martensitic stainless steel material,
a number ratio of Mg oxides having an equivalent circular diameter of 2.0 μm or more with respect to Ca oxides having an equivalent circular diameter of 2.0 μm or more, Ca sulfides having an equivalent circular diameter of 2.0 μm or more, and the Mg oxides having an equivalent circular diameter of 2.0 μm or more is 45.0% or more;

$$0.0010 \leq \text{Ca} + \text{Mg} \leq 0.0050 \dots (1)$$

where, a content of a corresponding element in percent by mass is substituted for each symbol of an element in Formula (1).

[2] The martensitic stainless steel material according to [1], containing one or more elements selected from a group consisting of:

Cu: 0.01 to 3.50%,
 Nb: 0.01 to 0.50%,
 Zr: 0.001 to 0.050%,
 W: 0.01 to 2.00%,
 B: 0.0001 to 0.0050%, and
 rare earth metal: 0.0001 to 0.0050%.

[3] The martensitic stainless steel material according to [1] or [2], wherein:

within ranges of contents of elements of the martensitic stainless steel material, contents of the elements satisfy Formula (2); and
 in the martensitic stainless steel material,
 a total number density of the Ca oxides having an equivalent circular diameter of 2.0 μm or more, the Ca sulfides having an equivalent circular diameter of 2.0 μm or more, and the Mg oxides having an equivalent circular diameter of 2.0 μm or more is 1000 / cm^2 or more;

$$\text{Ca/S} \geq 0.80 \dots (2)$$

where, a content of a corresponding element in percent by mass is substituted for each symbol of an element in Formula (2).

[0025] The shape of the martensitic stainless steel material according to the present embodiment is not particularly limited. The martensitic stainless steel material according to the present embodiment may be a steel pipe, may be a round steel bar (solid material), or may be a steel plate. Note that, the term "round steel bar" refers to a steel bar in which a cross section in a direction perpendicular to the axial direction is a circular shape. Further, the steel pipe may be a seamless steel pipe or may be a welded steel pipe.

[0026] Hereunder, the martensitic stainless steel material according to the present embodiment is described in detail. The symbol "%" in relation to an element means mass percent unless otherwise stated. Further, in the following description, the martensitic stainless steel material is also referred to as simply "steel material".

[Chemical composition]

[0027] The martensitic stainless steel material according to the present embodiment contains the following elements.

C: 0.030% or less

[0028] Carbon (C) is unavoidably contained. That is, the lower limit of the content of C is more than 0%. C increases hardenability of the steel material and increases the strength of the steel material. On the other hand, if the content of C is too high, even if the contents of other elements are within the range of the present embodiment, the strength of the steel material will be too high. As a result, the corrosion resistance of the steel material will decrease. Therefore, the content of C is to be 0.030% or less. A preferable upper limit of the content of C is 0.028%, more preferably is 0.025%, further preferably is 0.020%, and further preferably is 0.018%. The content of C is preferably as low as possible. However, extremely reducing the content of C will increase the production cost. Therefore, when taking industrial production into consideration, a preferable lower limit of the content of C is 0.001%, more preferably is 0.003%, and further preferably is 0.005%.

Si: 1.00% or less

[0029] Silicon (Si) is unavoidably contained. That is, the lower limit of the content of Si is more than 0%. Si deoxidizes the steel. On the other hand, if the content of Si is too high, even if the contents of other elements are within the range of the present embodiment, hot workability of the steel material will decrease. Therefore, the content of Si is to be 1.00% or less. A preferable lower limit of the content of Si for effectively obtaining the aforementioned advantageous effect is 0.01%, more preferably is 0.05%, further preferably is 0.10%, and further preferably is 0.15%. A preferable upper limit of the content of Si is 0.80%, more preferably is 0.70%, further preferably is 0.60%, further preferably is 0.50%, and further preferably is 0.45%.

Mn: 1.00% or less

[0030] Manganese (Mn) is unavoidably contained. That is, the lower limit of the content of Mn is more than 0%. Mn increases the hardenability of the steel material and increases the strength of the steel material. On the other hand, if the content of Mn is too high, even if the contents of other elements are within the range of the present embodiment, the corrosion resistance of the steel material will decrease. Therefore, the content of Mn is to be 1.00% or less. A preferable lower limit of the content of Mn for effectively obtaining the aforementioned advantageous effect is 0.01%, more preferably is 0.05%, further preferably is 0.10%, and further preferably is 0.15%. A preferable upper limit of the content of Mn is 0.90%, more preferably is 0.80%, further preferably is 0.70%, and further preferably is 0.60%.

P: 0.030% or less

[0031] Phosphorus (P) is an impurity that is unavoidably contained. That is, the lower limit of the content of P is more than 0%. If the content of P is too high, even if the contents of other elements are within the range of the present embodiment, P will segregate at grain boundaries and the corrosion resistance of the steel material will decrease. Therefore, the content of P is to be 0.030% or less. A preferable upper limit of the content of P is 0.025%, more preferably is 0.020%, and further preferably is 0.018%. The content of P is preferably as low as possible. However, extremely reducing the content of P will raise the production cost. Accordingly, when taking industrial production into consideration, a preferable lower limit of the content of P is 0.001%, more preferably is 0.002%, and further preferably is 0.003%.

S: 0.0050% or less

[0032] Sulfur (S) is an impurity that is unavoidably contained. That is, the lower limit of the content of S is more than 0%. If the content of S is too high, even if the contents of other elements are within the range of the present embodiment, S will segregate at grain boundaries and hot workability of the steel material will decrease. Therefore, the content of S is to be 0.0050% or less. A preferable upper limit of the content of S is 0.0040%, more preferably is 0.0030%, further preferably is 0.0025%, and further preferably is 0.0020%. The content of S is preferably as low as possible. However, extremely reducing the content of S will raise the production cost. Accordingly, when taking industrial production into consideration, a preferable lower limit of the content of S is 0.0001%, more preferably is 0.0003%, and further preferably is 0.0005%.

Cr: 11.00 to 14.00%

[0033] Chromium (Cr) forms a passive film on the surface of the steel material and thereby increases the corrosion resistance of the steel material. If the content of Cr is too low, even if the contents of other elements are within the range of the present embodiment, the aforementioned advantageous effect will not be sufficiently obtained. On the other hand, if the content of Cr is too high, even if the contents of other elements are within the range of the present embodiment, in some cases ferrite will be included in the microstructure, and it will be difficult to secure sufficient strength. Therefore, the content of Cr is to be within the range of 11.00 to 14.00%. A preferable lower limit of the content of Cr is 11.20%, more preferably is 11.40%, further preferably is 11.60%, further preferably is 11.80%, and further preferably is 12.00%. A preferable upper limit of the content of Cr is 13.80%, more preferably is 13.60%, and further preferably is 13.50%.

Ni: 4.00 to 7.50%

[0034] Nickel (Ni) increases hardenability of the steel material and increases the yield strength of the steel material. Ni also increases hot workability of the steel material. If the content of Ni is too low, even if the contents of other elements are within the range of the present embodiment, the aforementioned advantageous effects will not be sufficiently obtained. On the other hand, if the content of Ni is too high, even if the contents of other elements are within the range of the present embodiment, in some cases the corrosion resistance of the steel material may decrease. Therefore, the content of Ni is to be 4.00 to 7.50%. A preferable lower limit of the content of Ni is 4.20%, more preferably is 4.50%, further preferably is 5.00%, further preferably is 5.20%, further preferably is 5.30%, and further preferably is 5.50%. A preferable upper limit of the content of Ni is 7.40%, more preferably is 7.20%, further preferably is 7.00%, and further preferably is 6.50%.

Mo: 1.50 to 4.50%

[0035] Molybdenum (Mo) stabilizes the passive film and thereby increases the corrosion resistance of the steel material. If the content of Mo is too low, even if the contents of other elements are within the range of the present embodiment, the aforementioned advantageous effect will not be sufficiently obtained. On the other hand, if the content of Mo is too high, even if the contents of other elements are within the range of the present embodiment, it will be difficult to stabilize

austenite. As a result, in some cases a large amount of ferrite will be included in the microstructure after tempering and the corrosion resistance of the steel material will decrease. Therefore, the content of Mo is to be 1.50 to 4.50%. A preferable lower limit of the content of Mo is 1.80%, more preferably is 2.00%, and further preferably is 2.30%. A preferable upper limit of the content of Mo is 4.30%, more preferably is 4.00%, and further preferably is 3.80%.

Co: 0.01 to 0.50%

[0036] Cobalt (Co) stabilizes the passive film and increases the corrosion resistance of the steel material. Co also increases hardenability of the steel material and raises the yield strength of the steel material. If the content of Co is too low, even if the contents of other elements are within the range of the present embodiment, the aforementioned advantageous effects will not be sufficiently obtained. On the other hand, if the content of Co is too high, even if the contents of other elements are within the range of the present embodiment, toughness of the steel material will decrease. Therefore, the content of Co is to be 0.01 to 0.50%. A preferable lower limit of the content of Co is 0.02%, more preferably is 0.03%, and further preferably is 0.05%. A preferable upper limit of the content of Co is 0.45%, more preferably is 0.40%, and further preferably is 0.35%.

Ti: 0.05 to 0.30%

[0037] Titanium (Ti) combines with C and/or N to form carbides or nitrides. As a result, the yield strength of the steel material is increased. If the content of Ti is too low, even if the contents of other elements are within the range of the present embodiment, the aforementioned advantageous effect will not be sufficiently obtained. On the other hand, if the content of Ti is too high, even if the contents of other elements are within the range of the present embodiment, the strength of the steel material will be too high and the corrosion resistance of the steel material will decrease. Therefore, the content of Ti is to be 0.05 to 0.30%. A preferable lower limit of the content of Ti is 0.06%, and more preferably is 0.08%. A preferable upper limit of the content of Ti is 0.25%, more preferably is 0.20%, and further preferably is 0.18%.

V: 0.01 to 1.00%

[0038] Vanadium (V) increases hardenability of the steel material and raises the yield strength of the steel material. If the content of V is too low, even if the contents of other elements are within the range of the present embodiment, the aforementioned advantageous effect will not be sufficiently obtained. On the other hand, if the content of V is too high, even if the contents of other elements are within the range of the present embodiment, the strength of the steel material will be too high and the corrosion resistance of the steel material will decrease. Therefore, the content of V is to be 0.01 to 1.00%. A preferable lower limit of the content of V is 0.02%, and more preferably is 0.04%. A preferable upper limit of the content of V is 0.80%, and more preferably is 0.60%.

Ca: 0.0005 to 0.0050%

[0039] Calcium (Ca) immobilizes S in the steel material as a sulfide to make it harmless, and thereby improves hot workability of the steel material. If the content of Ca is too low, even if the contents of other elements are within the range of the present embodiment, the aforementioned advantageous effect will not be sufficiently obtained. On the other hand, if the content of Ca is too high, even if the contents of other elements are within the range of the present embodiment, coarse Ca oxides will be formed in the steel material and the corrosion resistance of the steel material will decrease. Therefore, the content of Ca is to be 0.0005 to 0.0050%. A preferable lower limit of the content of Ca is 0.0006%, more preferably is 0.0008%, and further preferably is 0.0010%. A preferable upper limit of the content of Ca is 0.0045%, more preferably is 0.0040%, further preferably is 0.0035%, further preferably is 0.0030%, and further preferably is 0.0025%.

Mg: 0.0005 to 0.0050%

[0040] Magnesium (Mg) immobilizes O in the steel material as an oxide to make it harmless, and thereby improves the corrosion resistance of the steel material. If the content of Mg is too low, even if the contents of other elements are within the range of the present embodiment, the aforementioned advantageous effect will not be sufficiently obtained. On the other hand, if the content of Mg is too high, even if the contents of other elements are within the range of the present embodiment, coarse Mg oxides will be formed in the steel material and the corrosion resistance of the steel material will decrease. Therefore, the content of Mg is to be 0.0005 to 0.0050%. A preferable lower limit of the content of Mg is 0.0006%, more preferably is 0.0007%, and further preferably is 0.0008%. A preferable upper limit of the content of Mg is 0.0045%, more preferably is 0.0040%, and further preferably is 0.0035%.

Al: 0.001 to 0.100%

[0041] Aluminum (Al) deoxidizes the steel. If the content of Al is too low, even if the contents of other elements are within the range of the present embodiment, the aforementioned advantageous effect will not be sufficiently obtained. On the other hand, if the content of Al is too high, even if the contents of other elements are within the range of the present embodiment, coarse oxides will form and the corrosion resistance of the steel material will decrease. Therefore, the content of Al is to be 0.001 to 0.100%. A preferable lower limit of the content of Al is 0.005%, more preferably is 0.010%, and further preferably is 0.015%. A preferable upper limit of the content of Al is 0.080%, more preferably is 0.060%, further preferably is 0.055%, further preferably is 0.050%, and further preferably is 0.040%. As used in the present description, the term "content of Al" means the content of sol. Al (acid-soluble Al).

N: 0.0500% or less

[0042] Nitrogen (N) is unavoidably contained. That is, the lower limit of the content of N is more than 0%. N combines with Ti to form fine Ti nitrides. As a result, the yield strength of the steel material is increased. On the other hand, if the content of N is too high, even if the contents of other elements are within the range of the present embodiment, coarse nitrides will be formed and the corrosion resistance of the steel material will decrease. Therefore, the content of N is to be 0.0500% or less. A preferable upper limit of the content of N is 0.0450%, more preferably is 0.0400%, further preferably is 0.0350%, and further preferably is 0.0300%. A preferable lower limit of the content of N for more effectively obtaining the aforementioned advantageous effect is 0.0015%, more preferably is 0.0020%, further preferably is 0.0030%, and further preferably is 0.0040%.

O: 0.0500% or less

[0043] Oxygen (O) is an impurity that is unavoidably contained. That is, the lower limit of the content of O is more than 0%. O forms oxides and reduces the corrosion resistance of the steel material. Accordingly, if the content of O is too high, even if the contents of other elements are within the range of the present embodiment, the corrosion resistance of the steel material will markedly decrease. Therefore, the content of O is to be 0.0500% or less. A preferable upper limit of the content of O is 0.0400%, more preferably is 0.0300%, and further preferably is 0.0200%. The content of O is preferably as low as possible. However, extremely reducing the content of O will raise the production cost. Therefore, when taking industrial production into consideration, a preferable lower limit of the content of O is 0.0005%, more preferably is 0.0010%, and further preferably is 0.0015%.

[0044] The balance in the martensitic stainless steel material according to the present embodiment is Fe and impurities. Here, the term "impurities" refers to elements which, when industrially producing the steel material, are mixed in from ore or scrap that is used as the raw material or from the production environment or the like, and which are not intentionally contained but are allowed within a range that does not adversely affect the martensitic stainless steel material according to the present embodiment.

[Optional elements]

[0045] The martensitic stainless steel material according to the present embodiment may further contain one or more elements selected from the group consisting of Cu, Nb, and Zr in lieu of a part of Fe. These elements are optional elements, and each of these elements increases the strength of the steel material.

Cu: 0 to 3.50%

[0046] Copper (Cu) is an optional element, and need not be contained. That is, the content of Cu may be 0%. When contained, Cu increases hardenability of the steel material and raises the yield strength of the steel material. If even a small amount of Cu is contained, the aforementioned advantageous effect will be obtained to a certain extent. On the other hand, if the content of Cu is too high, even if the contents of other elements are within the range of the present embodiment, hot workability of the steel material will decrease. Therefore, the content of Cu is to be 0 to 3.50%. A preferable lower limit of the content of Cu is more than 0%, more preferably is 0.01%, further preferably is 0.05%, and further preferably is 0.10%. A preferable upper limit of the content of Cu is 3.30%, more preferably is 3.10%, further preferably is 2.90%, and further preferably is 2.70%. Note that, as mentioned below, the lower limit of the content of Cu may be 0.50%. In this case, a further preferable lower limit of the content of Cu is 0.60%, further preferably is 0.65%, and further preferably is 0.70%. Also, as mentioned below, the upper limit of the content of Cu may be less than 0.50%. In this case, a further preferable lower limit of the content of Cu is 0.45%, further preferably is 0.43%, and further preferably is 0.40%.

Nb: 0 to 0.50%

[0047] Niobium (Nb) is an optional element, and need not be contained. That is, the content of Nb may be 0%. When contained, Nb combines with C and/or N to form carbides and/or carbo-nitrides. As a result, the yield strength of the steel material is increased. If even a small amount of Nb is contained, the aforementioned advantageous effect will be obtained to a certain extent. On the other hand, if the content of Nb is too high, even if the contents of other elements are within the range of the present embodiment, carbides and/or carbo-nitrides will be excessively formed and the corrosion resistance of the steel material will decrease. Therefore, the content of Nb is to be 0 to 0.50%. A preferable lower limit of the content of Nb is more than 0%, more preferably is 0.01%, and further preferably is 0.02%. A preferable upper limit of the content of Nb is 0.45%, more preferably is 0.40%, further preferably is 0.35%, further preferably is 0.20%, and further preferably is 0.10%.

Zr: 0 to 0.050%

[0048] Zirconium (Zr) is an optional element, and need not be contained. That is, the content of Zr may be 0%. When contained, Zr forms carbides and/or carbo-nitrides. As a result, the yield strength of the steel material is increased. If even a small amount of Zr is contained, the aforementioned advantageous effect will be obtained to a certain extent. On the other hand, if the content of Zr is too high, even if the contents of other elements are within the range of the present embodiment, carbides and/or carbo-nitrides will be excessively formed and the corrosion resistance of the steel material will decrease. Therefore, the content of Zr is to be 0 to 0.050%. A preferable lower limit of the content of Zr is more than 0%, more preferably is 0.001%, and further preferably is 0.002%. A preferable upper limit of the content of Zr is 0.045%, more preferably is 0.040%, further preferably is 0.030%, further preferably is 0.020%, and further preferably is 0.010%.

[0049] The martensitic stainless steel material according to the present embodiment may also contain W in lieu of a part of Fe.

W: 0 to 2.00%

[0050] Tungsten (W) is an optional element, and need not be contained. That is, the content of W may be 0%. When contained, W stabilizes the passive film and increases the corrosion resistance of the steel material. If even a small amount of W is contained, the aforementioned advantageous effect will be obtained to a certain extent. On the other hand, if the content of W is too high, even if the contents of other elements are within the range of the present embodiment, coarse carbides may be formed and the corrosion resistance of the steel material may decrease. Therefore, the content of W is to be 0 to 2.00%. A preferable lower limit of the content of W is more than 0%, more preferably is 0.01%, further preferably is 0.03%, further preferably is 0.05%, and further preferably is 0.10%. A preferable upper limit of the content of W is 1.70%, more preferably is 1.50%, further preferably is 1.00%, further preferably is 0.60%, further preferably is 0.50%, and further preferably is 0.40%.

[0051] The martensitic stainless steel material according to the present embodiment may further contain one or more elements selected from the group consisting of B and rare earth metal (REM) in lieu of a part of Fe. These elements are optional elements, and each of these elements increases hot workability of the steel material.

B: 0 to 0.0050%

[0052] Boron (B) is an optional element, and need not be contained. That is, the content of B may be 0%. When contained, B strengthens the grain boundaries and increases hot workability of the steel material. If even a small amount of B is contained, the aforementioned advantageous effect will be obtained to a certain extent. On the other hand, if the content of B is too high, even if the contents of other elements are within the range of the present embodiment, Cr carbides will form and the corrosion resistance of the steel material will decrease. Therefore, the content of B is to be 0 to 0.0050%. A preferable lower limit of the content of B is more than 0%, more preferably is 0.0001%, and further preferably is 0.0002%. A preferable upper limit of the content of B is 0.0045%, more preferably is 0.0040%, and further preferably is 0.0035%.

Rare earth metal (REM): 0 to 0.0050%

[0053] Rare earth metal (REM) is an optional element, and need not be contained. That is, the content of REM may be 0%. When contained, REM controls the morphology of inclusions and increases hot workability of the steel material. If even a small amount of REM is contained, the aforementioned advantageous effect will be obtained to a certain extent. On the other hand, if the content of REM is too high, even if the contents of other elements are within the range of the present embodiment, coarse oxides will be formed and the corrosion resistance of the steel material will decrease. Therefore, the

content of REM is to be 0 to 0.0050%. A preferable lower limit of the content of REM is more than 0%, more preferably is 0.0001%, further preferably is 0.0005%, and further preferably is 0.0010%. A preferable upper limit of the content of REM is 0.0045%, more preferably is 0.0040%, further preferably is 0.0035%, and further preferably is 0.0025%.

[0054] Note that, in the present description the term "REM" means one or more types of element selected from the group consisting of scandium (Sc) which is the element with atomic number 21, yttrium (Y) which is the element with atomic number 39, and the elements from lanthanum (La) with atomic number 57 to lutetium (Lu) with atomic number 71 that are lanthanoids. In the present description the term "content of REM" refers to the total content of these elements.

[0055] Preferably, the martensitic stainless steel material according to the present embodiment has the aforementioned chemical composition, in addition, the content of Cu is 0.50% or more and further the content of W is 0.01% or more. In this case, the steel material has more excellent corrosion resistance in a corrosive environment in which SO_x or NO_x is mixed. More specifically, among the martensitic stainless steel material according to the present embodiment, in the case where the chemical composition consists of, in mass%, C: 0.030% or less, Si: 1.00% or less, Mn: 1.00% or less, P: 0.030% or less, S: 0.0050% or less, Cr: 11.00 to 14.00%, Ni: 4.00 to 7.50%, Mo: 1.50 to 4.50%, Cu: 0.50 to 3.50%, Co: 0.01 to 0.50%, W: 0.01 to 2.00%, Ti: 0.05 to 0.30%, V: 0.01 to 1.00%, Ca: 0.0005 to 0.0050%, Mg: 0.0005 to 0.0050%, Al: 0.001 to 0.100%, N: 0.0500% or less, O: 0.0500% or less, Nb: 0 to 0.50%, Zr: 0 to 0.050%, B: 0 to 0.0050%, rare earth metal: 0 to 0.0050%, and the balance: Fe and impurities, the steel material has yield strength of 862 MPa or more and more excellent corrosion resistance in a corrosive environment in which SO_x or NO_x is mixed.

[0056] In other words, the martensitic stainless steel material according to the present embodiment may have the chemical composition consists of, in mass%, C: 0.030% or less, Si: 1.00% or less, Mn: 1.00% or less, P: 0.030% or less, S: 0.0050% or less, Cr: 11.00 to 14.00%, Ni: 4.00 to 7.50%, Mo: 1.50 to 4.50%, Co: 0.01 to 0.50%, Ti: 0.05 to 0.30%, V: 0.01 to 1.00%, Ca: 0.0005 to 0.0050%, Mg: 0.0005 to 0.0050%, Al: 0.001 to 0.100%, N: 0.0500% or less, O: 0.0500% or less, Cu: 0 to less than 0.50%, Nb: 0 to 0.50%, Zr: 0 to 0.050%, W: 0 to 2.00%, B: 0 to 0.0050%, rare earth metal: 0 to 0.0050%, and the balance: Fe and impurities.

[Formula (1)]

[0057] On the premise that the martensitic stainless steel material according to the present embodiment has the aforementioned chemical composition, the martensitic stainless steel material according to the present embodiment satisfies the following Formula (1). As a result, on the condition that the other requirements of the present embodiment are satisfied, the martensitic stainless steel material according to the present embodiment has high strength and has excellent corrosion resistance in a corrosive environment in which SO_x or NO_x is mixed.

$$0.0010 \leq \text{Ca} + \text{Mg} \leq 0.0050 \dots (1)$$

[0058] Where, a content of a corresponding element in percent by mass is substituted for each symbol of an element in Formula (1).

[0059] Fn1 (= Ca+Mg) is an index relating to Ca oxides and Mg oxides. If Fn1 is too low, Ca and Mg cannot sufficiently immobilize O as an oxide, and O remains in the steel material in a partially dissolved state. On the other hand, if Fn1 is too high, Mg oxides will be modified by Ca, and the number ratio of coarse Mg oxides with respect to the specific inclusions may decrease. Therefore, in the present embodiment, on the premise of having the aforementioned chemical composition, Fn1 is to be within the range of 0.0010 to 0.0050.

[0060] A preferable lower limit of Fn1 is 0.0012, and more preferably is 0.0015. A preferable upper limit of Fn1 is 0.0048, and more preferably is 0.0045.

[Yield strength]

[0061] In addition to having the aforementioned chemical composition, the martensitic stainless steel material according to the present embodiment satisfies Formula (1), and further the number ratio of coarse Mg oxides with respect to the specific inclusions is made 45.0% or more. As a result, even though the martensitic stainless steel material according to the present embodiment has a yield strength of 862 MPa or more, the martensitic stainless steel material has excellent corrosion resistance in a corrosive environment in which SO_x or NO_x is mixed.

[0062] That is, the yield strength of the martensitic stainless steel material according to the present embodiment is 862 MPa (125 ksi) or more. Although the upper limit of the yield strength of the steel material is not particularly limited, the upper limit of the yield strength of the steel material of the present embodiment is, for example, 1034 MPa (150 ksi). A further preferable upper limit of the yield strength of the steel material is 1000 MPa (145 ksi). As used herein, the term "yield strength" means 0.2% offset proof stress (MPa) obtained by a tensile test at normal temperature (24 ± 3°C) in conformity with ASTM E8/E8M (2021) that is described hereunder.

[0063] Specifically, in the present embodiment, the yield strength is determined by the following method. First, a tensile test specimen is prepared from the martensitic stainless steel material according to the present embodiment. The size of the tensile test specimen is not particularly limited. For example, a round bar tensile test specimen in which the diameter of the parallel portion is 8.9 mm and the gage length is 35.6 mm is used as the tensile test specimen. If the steel material is a steel pipe, the tensile test specimen is prepared from a central position of the wall thickness. In this case, the longitudinal direction of the tensile test specimen is to be made parallel to the axial direction of the steel pipe. If the steel material is a round steel bar, the tensile test specimen is prepared from an R/2 position. Note that, in the present description, the term "R/2 position" of a round steel bar means the center position of a radius R in a cross section perpendicular to the axial direction of the round steel bar. Further, in this case, the longitudinal direction of the tensile test specimen is to be made parallel to the axial direction of the round steel bar. If the steel material is a steel plate, the tensile test specimen is prepared from a central position of the thickness. In this case, the longitudinal direction of the tensile test specimen is to be made parallel to the rolling elongation direction of the steel plate. A tensile test is conducted at normal temperature ($24 \pm 3^\circ\text{C}$) in accordance with ASTM E8/E8M (2021) using the prepared tensile test specimen, and the 0.2% offset proof stress (MPa) is determined. The determined 0.2% offset proof stress is defined as the yield strength (MPa).

[Number ratio of coarse Mg oxides]

[0064] In addition to having the aforementioned chemical composition, the martensitic stainless steel material according to the present embodiment satisfies Formula (1), and in addition, in the martensitic stainless steel material, a number ratio of coarse Mg oxides with respect to the specific inclusions is 45.0% or more. As a result, the martensitic stainless steel material according to the present embodiment has a yield strength of 862 MPa or more, and has excellent corrosion resistance in a corrosive environment in which SO_x or NO_x is mixed.

[0065] As mentioned above, Ca oxides having an equivalent circular diameter of 2.0 μm or more are also referred to as "coarse Ca oxides". Ca sulfides having an equivalent circular diameter of 2.0 μm or more are also referred to as "coarse Ca sulfides". Further, Mg oxides having an equivalent circular diameter of 2.0 μm or more are also referred to as "coarse Mg oxides". In addition, coarse Ca oxides, coarse Ca sulfides, and coarse Mg oxides are also collectively referred to as "specific inclusions".

[0066] Here, coarse Ca oxides are liable to serve as a starting point for pitting in a corrosive environment in which SO_x or NO_x is mixed. Therefore, in the present embodiment, the ratio of coarse Mg oxides among the specific inclusions is increased, and the number of coarse Ca oxides is reduced. As a result, excellent corrosion resistance can be obtained even in a corrosive environment in which SO_x or NO_x is mixed. Therefore, in the present embodiment, on the premise of having the aforementioned chemical composition and satisfying Formula (1), the number ratio of coarse Mg oxides with respect to the specific inclusions is to be 45.0% or more.

[0067] In the present embodiment, a preferable lower limit of the number ratio of coarse Mg oxides with respect to the specific inclusions is 46.0%, more preferably is 48.0%, and further preferably is 50.0%. In the present embodiment, the upper limit of the number ratio of coarse Mg oxides with respect to the specific inclusions is not particularly limited, and for example may be 99.0%.

[0068] In the present embodiment, the number ratio of coarse Mg oxides with respect to the specific inclusions is determined by the following method. First, the total number density of coarse Ca oxides and coarse Ca sulfides, and the number density of coarse Mg oxides are determined from the martensitic stainless steel material according to the present embodiment. Here, in the martensitic stainless steel material according to the present embodiment, it is difficult to clearly separate coarse Ca oxides from coarse Ca sulfides. Further, there is no necessity to determine the respective number densities of coarse Ca oxides and coarse Ca sulfides. Therefore, in the present embodiment, the total number density of coarse Ca oxides and coarse Ca sulfides, and the number density of coarse Mg oxides are determined.

[0069] Specifically, a test specimen in which a face including the rolling elongation direction and the rolling reduction direction is adopted as an observation surface is prepared from the martensitic stainless steel material according to the present embodiment. If the steel material is a steel pipe, a test specimen in which a face including the pipe axis direction and the wall thickness direction is adopted as an observation surface is prepared from a central position of the wall thickness. If the steel material is a round steel bar, a test specimen which includes an R/2 position at the center thereof and in which a face including the axial direction and the radial direction at the relevant cross section is adopted as an observation surface is prepared. If the steel material is a steel plate, a test specimen in which a face including the rolling elongation direction and the plate thickness direction is adopted as an observation surface is prepared from a central position of the thickness. The size of the test specimen is not particularly limited, and for example the test specimen is prepared so as to include an observation surface having dimensions of 22 mm $\times$ 22 mm.

[0070] The prepared test specimen is embedded in resin, and the observation surface is polished. On the observation surface after polishing, an arbitrary 10 visual fields are observed. The area of each visual field is set to, for example, 100 mm² (10 mm $\times$ 10 mm). On the observation surface, particles having an equivalent circular diameter of 2.0 μm or more are identified based on contrast. The equivalent circular diameter of each particle can be determined by image analysis. The

identified particles having an equivalent circular diameter of 2.0 μm or more are subjected to an element concentration analysis (EDS analysis). In the EDS analysis, contents are determined with an accelerating voltage of 20 kV for N, O, Mg, Al, Si, P, S, Ca, Ti, Cr, Mn, Fe, Cu, and Nb as elements to be analyzed.

[0071] Based on the results of the EDS analysis of each particle, particles in which, in mass%, the content of Ca is 3% or more, the content of Mg is 5% or less, the content of Ti is less than 30%, and content of Al is less than 30% are identified as "coarse Ca oxides or coarse Ca sulfides". In addition, based on the results of the EDS analysis of each particle, particles in which, in mass%, the content of Mg is more than 5%, the content of S is less than 15%, the content of Ti is less than 30%, and the content of Al is less than 30% are identified as "coarse Mg oxides".

[0072] The total number density of coarse Ca oxides and coarse Ca sulfides ($/\text{cm}^2$) is determined based on the total number of coarse Ca oxides or coarse Ca sulfides identified in the 10 visual fields, and the total area of the 10 visual fields. Similarly, the number density of coarse Mg oxides ($/\text{cm}^2$) is determined based on the total number of coarse Mg oxides identified in the 10 visual fields, and the total area of the 10 visual fields. Note that, in the present embodiment, a value obtained by rounding off the first decimal place of the obtained numerical value is adopted as the total number density of coarse Ca oxides and coarse Ca sulfides, and the number density of coarse Mg oxides, respectively.

[0073] The total of the obtained total number density of coarse Ca oxides and coarse Ca sulfides ($/\text{cm}^2$) and number density of coarse Mg oxides ($/\text{cm}^2$) is defined as the total number density ($/\text{cm}^2$) of the specific inclusions. In addition, a ratio of the number density of coarse Mg oxides ($/\text{cm}^2$) to the obtained total number density ($/\text{cm}^2$) of the specific inclusions is determined as a percentage, and is defined as the number ratio (%) of the coarse Mg oxides with respect to the specific inclusions. Note that, the number density of the specific inclusions and of the coarse Mg oxides can be determined using an apparatus in which a scanning electron microscope is provided with a composition analysis function (SEM-EDS apparatus). For example, automated inclusion analysis equipment having the trade name "Metals Quality Analyzer" manufactured by FEI Company (ASPEX Corporation) can be used as the SEM-EDS apparatus.

[Corrosion resistance]

[0074] The martensitic stainless steel material according to the present embodiment has the aforementioned chemical composition, satisfies Formula (1), and has a yield strength of 862 MPa or more, and furthermore, in the martensitic stainless steel material, the number ratio of coarse Mg oxides with respect to the specific inclusions is 45.0% or more. As a result, the martensitic stainless steel material according to the present embodiment has excellent corrosion resistance in a corrosive environment in which SOx or NOx is mixed. In the present embodiment, the phrase "has excellent corrosion resistance in a corrosive environment in which SOx or NOx is mixed" means that, in a corrosion rate test performed at 150°C described hereunder, the corrosion rate is 0.100 mm/year or less, and pitting is not confirmed.

[0075] Specifically, the martensitic stainless steel material according to the present embodiment is subjected to a corrosion rate test. Specifically, a test specimen for a corrosion rate test is prepared from the martensitic stainless steel material according to the present embodiment. If the steel material is a steel pipe, the test specimen is prepared from a central position of the wall thickness. In this case, the longitudinal direction of the test specimen is made parallel to the axial direction of the steel pipe. If the steel material is a round steel bar, the test specimen is prepared from the R/2 position. In this case, the longitudinal direction of the test specimen is made parallel to the axial direction of the round steel bar. If the steel material is a steel plate, the test specimen is prepared from a central position of the thickness. In this case, the longitudinal direction of the test specimen is made parallel to the rolling elongation direction of the steel plate. The test specimen is, for example, a test specimen having a length of 30 mm, a width of 20 mm, and a thickness of 2 mm.

[0076] The test specimen is inserted into an autoclave, and an aqueous solution containing 5.0% sodium chloride by mass is poured into the autoclave so as to immerse the test specimen in the aqueous solution. A gaseous mixture of SO₂, NO₂, and CO₂ is sealed under pressure in the autoclave to start the corrosion rate test. At such time, the total pressure of the gaseous mixture is made 130 bar, the SO₂ concentration in the gaseous mixture is made 10 ppm, and the NO₂ concentration in the gaseous mixture is made 10 ppm. Further, the test time of the corrosion rate test is set to 96 hours, and the temperature inside the autoclave during the test is maintained at 150°C.

[0077] The mass, density, and surface area of the test specimen after the 96 hours elapse are determined, and the corrosion rate (mm/year) of the test specimen is determined. Note that, in the present embodiment, a value obtained by rounding off the fourth decimal place of the obtained numerical value is adopted as the corrosion rate. In addition, the surface of the test specimen after 96 hours elapse is observed using a magnifying glass with a magnification of $\times 10$ to confirm the presence or absence of pitting. If the occurrence of pitting is suspected as a result of the observation with a magnifying glass, the surface of the test specimen is further observed using an optical microscope with a magnification of $\times 100$ to confirm the presence or absence of pitting. In the present embodiment, if the obtained corrosion rate is 0.100 mm/year or less and pitting is not confirmed, it is determined that the steel material has excellent corrosion resistance in a corrosive environment in which SOx or NOx is mixed.

[0078] As mentioned above, in the case where the martensitic stainless steel material according to the present embodiment has the aforementioned chemical composition, in addition, the content of Cu: 0.50 to 3.50%, and the content

of W: 0.01 to 2.00%, the steel material has more excellent corrosion resistance in a corrosive environment in which SO_x or NO_x is mixed. In the present embodiment, the phrase "has more excellent corrosion resistance in a corrosive environment in which SO_x or NO_x is mixed" means that, in a corrosion rate test performed at 175°C described hereunder, the corrosion rate is 0.100 mm/year or less, and pitting is not confirmed. Specifically, a corrosion rate test that is identical to the

[Microstructure]

[0079] The microstructure of the martensitic stainless steel material according to the present embodiment is mainly composed of martensite. As used herein, the phrase "mainly composed of martensite" means that the microstructure is composed of, in volume ratio, 0 to 5% of retained austenite and 0 to 5% of ferrite, and the balance is martensite. In the present description, the phrase "composed of retained austenite, ferrite, and martensite" means that the amount of any phase other than retained austenite, ferrite, and martensite is negligible. For example, in the chemical composition of the martensitic stainless steel material according to the present embodiment, the volume ratios of precipitates and inclusions are negligible as compared with the volume ratios of retained austenite, ferrite, and martensite. That is, the microstructure of the martensitic stainless steel material according to the present embodiment may contain minute amounts of precipitates, inclusions and the like, in addition to retained austenite, ferrite, and martensite.

[0080] If the microstructure of a steel material having the aforementioned chemical composition is mainly composed of martensite, on the condition that the other requirements of the present embodiment are satisfied, the steel material will have a yield strength of 862 MPa or more, and will have excellent corrosion resistance in a corrosive environment in which SO_x or NO_x is mixed. Therefore, in the present embodiment, in a case where, in addition to having the aforementioned chemical composition and satisfying the other requirements of the present embodiment, if a steel material has a yield strength of 862 MPa or more and has excellent corrosion resistance in a corrosive environment in which SO_x or NO_x is mixed, it is determined that the microstructure of the relevant steel material is composed of, in volume ratio, 0 to 5% of retained austenite and 0 to 5% of ferrite, with the balance being martensite.

[0081] Note that, when identifying the microstructure of a steel material by observation, the following method can be used. In this case, specifically, the volume ratio (%) of martensite in the microstructure of the steel material is determined by subtracting a volume ratio (%) of retained austenite determined by a method described hereunder and a volume ratio (%) of ferrite determined by a method described hereunder from 100%.

[Method for measuring volume ratio of retained austenite]

[0082] The volume ratio of retained austenite in the microstructure of the steel material is determined by an X-ray diffraction method. Specifically, a test specimen for measuring the volume ratio of retained austenite is prepared from the steel material according to the present embodiment. If the steel material is a steel pipe, the test specimen is taken from a central position of the wall thickness. If the steel material is a round steel bar, the test specimen is taken from an R/2 position.

[0083] If the steel material is a steel plate, the test specimen is taken from a central position of the thickness. The size of the test specimen is not particularly limited. The test specimen is for example, 15 mm × 15 mm × a thickness of 2 mm. If the steel material is a steel pipe, the thickness direction of the test specimen is the pipe diameter direction. If the steel material is a round steel bar, the thickness direction of the test specimen is the radial direction. If the steel material is a steel plate, the thickness direction of the test specimen is the plate thickness direction. Using the prepared test specimen, the X-ray diffraction intensity of each of the (110) plane of α phase (martensite), the (200) plane of α phase, the (211) plane of α phase, the (111) plane of γ phase (retained austenite), the (200) plane of γ phase, and the (220) plane of γ phase are measured, and an integrated intensity of the respective planes is calculated.

[0084] In the measurement of the X-ray diffraction intensity, the target of the X-ray diffraction apparatus is Co (Co K α radiation), and the output is set to 30 kV - 100 mA. The measurement angle (2 θ) is set to 45 to 105°. After calculation, the volume ratio V_y (%) of retained austenite is calculated using Formula (I) for combinations (3 × 3 = 9 pairs) of each plane of the α phase and each plane of the γ phase. Then, an average value of the volume ratios V_y of retained austenite of the nine pairs is defined as the volume ratio (%) of retained austenite.

$$V_{\gamma} = 100 / \{ 1 + (I_{\alpha} \times R_{\gamma}) / (I_{\gamma} \times R_{\alpha}) \} \dots (I)$$

[0085] Where, I α is the integrated intensity of α phase. R α is a crystallographic theoretical calculation value of α phase. I γ is the integrated intensity of γ phase. R γ is a crystallographic theoretical calculation value of γ phase. Values incorporated

into a retained γ quantitative analysis system belonging to RINT-TTR (product name) manufactured by Rigaku Corporation can be used for the values of $R\alpha$ and $R\gamma$ for each plane. Note that, a value obtained by rounding off the first decimal place of the obtained numerical value is adopted as the volume ratio of retained austenite.

[Method for measuring volume ratio of ferrite]

[0086] The volume ratio of ferrite in the microstructure of the steel material is determined by a point counting method. Specifically, a test specimen for measuring the volume ratio of ferrite is prepared from the steel material according to the present embodiment. If the steel material is a steel pipe, the test specimen is taken from a central position of the wall thickness. If the steel material is a round steel bar, the test specimen is taken from an R/2 position. If the steel material is a steel plate, the test specimen is taken from a central position of the thickness. Note that, the size of the test specimen is not particularly limited. Further, if the steel material is a steel pipe, a face that is parallel to the axial direction of the steel pipe is adopted as the observation surface of the test specimen. If the steel material is a round steel bar, a face that is parallel to the axial direction of the round steel bar is adopted as the observation surface of the test specimen. If the steel material is a steel plate, a face that is parallel to the rolling elongation direction of the steel plate is adopted as the observation surface of the test specimen. After the observation surface is mechanically polished, the observation surface is subjected to electrolytic etching to reveal the microstructure. The electrolytic etching is performed using a 30% sodium hydroxide aqueous solution as the electrolyte, at a current density of 1 A/cm², for an electrolysis time of 1 minute.

[0087] On the observation surface subjected to the electrolytic etching, 30 visual fields are observed using an optical microscope. Each observation visual field is set as a rectangle of 250 μm $\times$ 250 μm . Note that, the observation magnification is $\times 400$. Those skilled in the art can distinguish ferrite from other phases (retained austenite or martensite) based on contrast in each observation visual field. Therefore, ferrite in each observation visual field is identified based on contrast. The area fraction of the identified ferrite is determined by a point counting method conforming to ASTM E562 (2019).

[0088] Specifically, for each observation visual field, 20 vertical lines are drawn at regular intervals from the top end to the bottom end of the observation visual field. That is, the observation visual field is divided into 21 regions in the left-right direction by the 20 vertical lines. Further, for each observation visual field, 20 horizontal lines are also drawn at regular intervals from the left end to the right end of the observation visual field. That is, the observation visual field is divided into 21 regions in the vertical direction by the 20 horizontal lines. At this time, intersections between the vertical lines and the horizontal lines are called lattice points. That is, in each observation visual field, 400 lattice points are arranged at regular intervals. In accordance with ASTM E562 (2019), the lattice points that overlap with ferrite in the observation visual field are counted. The number of lattice points overlapping with ferrite obtained in the 30 visual fields is divided by the total number of lattice points ($400 \times 30 = 12000$), and the resultant value is defined as the ferrite area fraction. In the present embodiment, the area fraction of ferrite determined by the above method is defined as the volume ratio (%) of ferrite. Note that, a value obtained by rounding off the first decimal place of the obtained numerical value is adopted as the volume ratio of ferrite.

[0089] Using the volume ratio (%) of retained austenite obtained by the aforementioned X-ray diffraction method, and the volume ratio (%) of ferrite obtained by the aforementioned point counting method, the volume ratio (%) of martensite in the microstructure of the steel material is determined by the following formula.

$$\text{Volume ratio (\% of martensite)} = 100.0 - \{\text{volume ratio (\% of retained austenite)} + \text{volume ratio (\% of ferrite)}\}$$

[0090] As described above, the martensitic stainless steel material according to the present embodiment has the aforementioned chemical composition, satisfies Formula (1), has a yield strength of 862 MPa or more, and furthermore, in the martensitic stainless steel material, a number ratio of coarse Mg oxides with respect to the specific inclusions is 45.0% or more. As a result, the martensitic stainless steel material according to the present embodiment has high strength, and has excellent corrosion resistance in a corrosive environment in which SO_x or NO_x is mixed.

[Optional features]

[0091] The martensitic stainless steel material according to the present embodiment may have the features described hereunder. That is, the features described hereunder are optional features in the martensitic stainless steel material according to the present embodiment.

[Total number density of specific inclusions]

[0092] On the premise that the martensitic stainless steel material according to the present embodiment has the

aforementioned chemical composition, satisfies the aforementioned Formula (1), has a yield strength of 862 MPa or more, and satisfies a condition that the number ratio of coarse Mg oxides with respect to the specific inclusions is 45.0% or more, the total number density of the specific inclusions may be 1000 /cm² or more. In a case where the martensitic stainless steel material according to the present embodiment satisfies a condition that the total number density of the specific inclusions is 1000 /cm² or more, the martensitic stainless steel material according to the present embodiment also has excellent hot workability, in addition to having high strength, and excellent corrosion resistance in a corrosive environment in which SO_x or NO_x is mixed.

[0093] In a steel material having the aforementioned chemical composition, if it is attempted to immobilize O or S with Ca and Mg, oxides will be preferentially formed, and S is liable to remain in a dissolved state. On the other hand, if the total number density of the specific inclusions is raised, the solubility of S can be decreased and the hot workability of the steel material will increase. Therefore, in the martensitic stainless steel material according to the present embodiment, preferably the total number density of the specific inclusions is made 1000 /cm² or more.

[0094] In the present embodiment, a more preferable lower limit of the total number density of the specific inclusions is 1050 /cm², further preferably is 1100 /cm², and further preferably is 1150 /cm². In the present embodiment, the upper limit of the total number density of the specific inclusions is not particularly limited, and for example may be 3000 /cm².

[0095] Note that, the total number density of coarse Ca oxides and coarse Ca sulfides, and the number density of coarse Mg oxides are not particularly limited. The total number density of coarse Ca oxides and coarse Ca sulfides, for example, may be 10 to 1500 /cm², may be 30 to 1250 /cm², or may be 50 to 1000 /cm². The number density of coarse Mg oxides, for example, may be 450 to 3000 /cm², may be 500 to 2500 /cm², or may be 600 to 2000 /cm².

[Formula (2)]

[0096] On the premise that the martensitic stainless steel material according to the present embodiment has the aforementioned chemical composition, satisfies the aforementioned Formula (1), has a yield strength of 862 MPa or more, and satisfies a condition that a number ratio of coarse Mg oxides with respect to the specific inclusions is 45.0% or more, the martensitic stainless steel material may satisfy the following Formula (2). In a case where the martensitic stainless steel material according to the present embodiment satisfies Formula (2), the total number density of the specific inclusions can be stably raised to 1000 /cm² or more.

$$\text{Ca/S} \geq 0.80 \dots (2)$$

[0097] Where, a content of a corresponding element in percent by mass is substituted for each symbol of an element in Formula (2).

[0098] Let Fn2 be defined as $\text{Fn2} = \text{Ca/S}$. Fn2 is an index relating to Ca sulfides. By increasing Fn2, Ca can sufficiently immobilize S as a Ca sulfide. As a result, the total number density of the specific inclusions can be stably increased. Therefore, in the martensitic stainless steel material according to the present embodiment, on the premise of having the aforementioned chemical composition and satisfying the aforementioned Formula (1), preferably Fn2 is made 0.80 or more.

[0099] A more preferable lower limit of Fn2 is 0.85, further preferably is 0.90, and further preferably is 1.00. The upper limit of Fn2 is not particularly limited, and for example may be 20.00, may be 15.00, or may be 10.00.

[Hot workability]

[0100] Preferably, in addition to having the aforementioned chemical composition, the martensitic stainless steel material according to the present embodiment satisfies Formulae (1) and (2), has a yield strength of 862 MPa or more, the number ratio of coarse Mg oxides with respect to the specific inclusions is made 45.0% or more, and furthermore, the total number density of the specific inclusions is made 1000 /cm² or more. As a result, the martensitic stainless steel material according to the present embodiment not only has high strength and excellent corrosion resistance in a corrosive environment in which SO_x or NO_x is mixed, but also has excellent hot workability. In the present embodiment, the phrase "has excellent hot workability" means that a reduction value Ra obtained in a hot workability test described hereunder is 70% or more.

[0101] The martensitic stainless steel material according to the present embodiment is subjected to a hot workability test (Gleeble test). Specifically, a test specimen for a Gleeble test is prepared from a starting material obtained by a process for producing the martensitic stainless steel material according to the present embodiment. The starting material may be a cast piece or an ingot, and the cast piece may be a billet, may be a bloom, or may be a slab. Preferably, a cast piece or an ingot subjected to hot forging or blooming is used.

[0102] In the present embodiment, although a position in the starting material from which to prepare the test specimen

for a Gleeble test is not particularly limited, the test specimen is prepared in a manner so as to avoid a central portion of the starting material where segregation or a defect is liable to occur during solidification. The test specimen is, for example, a round bar specimen having a diameter of 10 mm and a length of 130 mm. The longitudinal direction of the test specimen is to be parallel to the direction in which hot working is performed on the starting material. For example, in a case where the starting material is a round billet, and piercing-rolling is performed as hot working, the longitudinal direction of the test specimen is to be parallel to the axial direction (rolling elongation direction) of the round billet.

[0103] The test specimen heated to 900°C is subjected to a tensile test at a strain rate of 10s^{-1} to cause the test specimen to break. A reduction value R_a (%) is determined based on the broken test specimen. Note that, in the present embodiment, a value obtained by rounding off the first decimal place of the obtained numerical value is adopted as the reduction value R_a . In the present embodiment, if the obtained reduction value R_a is 70% or more, it is determined that the steel material has excellent hot workability.

[Shape and uses of steel material]

[0104] As mentioned above, the shape of the martensitic stainless steel material according to the present embodiment is not particularly limited. Specifically, the martensitic stainless steel material according to the present embodiment may be a steel pipe, may be a round steel bar (solid material), or may be a steel plate. Further, the steel pipe may be a seamless steel pipe or may be a welded steel pipe. The martensitic stainless steel material according to the present embodiment, for example, is suitable for use in CCUS storage technology.

[Production method]

[0105] An example of a method for producing the martensitic stainless steel material according to the present embodiment will now be described. Note that, the production method described hereunder is an example, and a method for producing the martensitic stainless steel material according to the present embodiment is not limited to the production method described hereunder. That is, as long as the martensitic stainless steel material according to the present embodiment that is composed as described above can be produced, a method for producing the martensitic stainless steel material is not limited to the production method described hereunder. However, the production method described hereunder is a favorable method for producing the martensitic stainless steel material according to the present embodiment.

[0106] One example of a method for producing the martensitic stainless steel material according to the present embodiment includes a process of preparing a starting material (steelmaking process), a process of subjecting the starting material to hot working to produce an intermediate steel material (hot working process), and a process of subjecting the intermediate steel material to quenching and tempering (heat treatment process). Each of these processes is described in detail hereunder.

[Steelmaking process]

[0107] The steelmaking process includes a process of producing molten steel (refining process), and a process of producing a starting material by a casting process using the molten steel (starting material production process).

[Refining process]

[0108] In the refining process, first, a molten steel containing Cr is placed in a ladle, and the molten steel in the ladle is subjected to a decarburization treatment under atmospheric pressure (rough decarburization refining process). Slag is generated by the decarburization treatment in the rough decarburization refining process. The slag generated by the decarburization treatment floats on the liquid surface of the molten steel after the rough decarburization refining process. In the rough decarburization refining process, Cr in the molten steel is oxidized to form Cr_2O_3 . The Cr_2O_3 is absorbed into the slag. Therefore, a deoxidizer is added to the ladle to reduce Cr_2O_3 in the slag and recover Cr in the molten steel (Cr reduction treatment process). The rough decarburization refining process and the Cr reduction treatment process are carried out, for example, by an electric furnace process, a converter process, or an AOD (Argon Oxygen Decarburization) process. After the Cr reduction treatment process, the slag is removed from the molten steel (slag removal treatment process).

[0109] The molten steel after the slag removal treatment process is further subjected to a finishing decarburization treatment (finishing decarburization refining process). After the finishing decarburization refining process, a deoxidizer is added to the molten steel, and the Cr reduction treatment for reducing Cr_2O_3 in the slag is performed again (Cr reduction treatment process). The finishing decarburization refining process and the Cr reduction treatment process after the finishing decarburization refining process may be performed, for example, by the VOD (Vacuum Oxygen Decarburization)

process or may be performed by the RH (Ruhrstahl-Heraeus) process.

[0110] After the Cr reduction treatment process, the molten steel in the ladle is subjected to final composition adjustment and to temperature adjustment of the molten steel before the starting material production process (component adjustment process). The component adjustment process is performed, for example, by LT (Ladle Treatment). In the component adjustment process according to the present embodiment, preferably the molten steel temperature in the ladle is held at 1500 to 1700°C.

[0111] Preferably, in the component adjustment process according to the present embodiment, the addition of the elements is carried out in the following order. Specifically, Mg is added to the molten steel to form coarse Mg oxides in the molten steel. Thereafter, preferably Ca is added to the molten steel to form coarse Ca sulfides. The deoxidizing power of Ca in the molten steel is stronger than the deoxidizing power of Mg. Therefore, if Mg is added to the molten steel after Ca was added to the molten steel and coarse Ca oxides were formed, in some cases it may not be possible for coarse Mg oxides to be sufficiently formed. In such a case, in the produced martensitic stainless steel material, the number ratio of coarse Mg oxides with respect to the specific inclusions will be lowered, and excellent corrosion resistance will not be obtained in a corrosive environment in which SOx or NOx is mixed. Therefore, preferably, in the component adjustment process according to the present embodiment, Mg is added to the molten steel and then Ca is added to the molten steel.

[0112] In the component adjustment process according to the present embodiment, in addition, it is preferable to control the timing at which Ca is added after Mg was added to the molten steel, and the timing at which the molten steel is tapped after Ca was added thereto. Specifically, the time from when an elemental component is added to the molten steel until the added elemental component is uniformly dispersed in the molten steel is defined as a "uniform mixing time" τ . The uniform mixing time τ can be determined by the following Formula (A):

$$\tau = 800 \times \varepsilon^{-0.4} \dots (A)$$

where, ε represents the stirring power density of the molten steel in the LT, and is defined by Formula (B):

$$\varepsilon = 28.5(Q/W) \times T \times \log(1+H/1.48) \dots (B)$$

where, Q represents the top blowing gas flow rate (Nm³/min), W represents the molten steel mass (t), T represents the molten steel temperature (K), and H represents the depth of the molten steel in the ladle (steel bath depth) (m).

[0113] In the present description, in the component adjustment process, the time from when Mg is added to the molten steel and the uniform mixing time τ passes until Ca is added is defined as "holding time tA" (secs). Further, in the present description, in the component adjustment process, the time from when Ca is added to the molten steel and the uniform mixing time τ passes until the molten steel is tapped is defined as "holding time tB" (secs). Preferably, in the component adjustment process according to the present embodiment, the holding time tA (secs) and the holding time tB (secs) satisfy the following Formula (C).

$$tA/tB > 1.0 \dots (C)$$

[0114] Let FnC be defined as $FnC = tA/tB$. FnC is an index that indicates the state of oxide-based inclusions in the molten steel. In some cases, when FnC is small, Mg oxides are not sufficiently formed. Further, when FnC is small, in some cases Mg oxides are modified too much by Ca oxides, and the Mg oxides in the molten steel decrease. In addition, when FnC is small, in some cases Ca oxides and/or Ca sulfides become coarse and the Ca oxides and/or Ca sulfides in the molten steel decrease. In these cases, in the produced martensitic stainless steel material, in some cases the number ratio of coarse Mg oxides with respect to the specific inclusions is lowered and excellent corrosion resistance is not obtained in a corrosive environment in which SOx or NOx is mixed. Furthermore, in these cases, in the produced martensitic stainless steel material, the total number density of the specific inclusions may decrease.

[0115] Therefore, in the component adjustment process of the present embodiment, preferably FnC is made more than 1.0. In this case, in the produced martensitic stainless steel material, the number ratio of coarse Mg oxides with respect to the specific inclusions can be stably increased. Note that, an upper limit of FnC is not particularly limited, and for example, may be 10.0. Note that, as long as FnC is more than 1.0, the holding time tA from when Mg is added to the molten steel and the uniform mixing time τ passes until Ca is added, and the holding time tB from when Ca is added to the molten steel and the uniform mixing time τ passes until the molten steel is tapped are not particularly limited. The holding time tA may be, for example, 120 to 600 seconds. The holding time tB is, for example, 60 to less than 120 seconds. The starting material production process is described hereunder.

[Starting material production process]

[0116] A starting material (cast piece or ingot) is produced using the molten steel produced in the above-described refining process. Specifically, a cast piece is produced by a continuous casting process using the molten steel. The cast piece may be a slab, may be a bloom, or may be a billet. Alternatively, an ingot may be produced by an ingot-making process using the molten steel. The cast piece or ingot may be further subjected to blooming or the like to produce a billet. A starting material is produced by the above-described process. The hot working process is described in detail hereunder.

[Hot working process]

[0117] In the hot working process, the starting material is subjected to hot working to produce an intermediate steel material. If the steel material is a seamless steel pipe, the intermediate steel material corresponds to a hollow shell. If the steel material is a seamless steel pipe, first, a billet is heated in a heating furnace. Although not particularly limited, the heating temperature is, for example, 1100 to 1300°C. After the billet is extracted from the heating furnace, the billet is subjected to hot working to produce a hollow shell (seamless steel pipe). The method of hot working is not particularly limited, and it suffices to use a well-known method.

[0118] For example, the Mannesmann process may be performed as hot working to produce a hollow shell. In this case, a round billet is subjected to piercing-rolling using a piercing machine. When performing piercing-rolling, although not particularly limited, for example, the piercing ratio is 1.0 to 4.0. The round billet subjected to piercing-rolling is further subjected to hot rolling with a mandrel mill, a reducer, a sizing mill or the like to produce a hollow shell. The cumulative reduction of area in the hot working process is, for example, 20 to 70%.

[0119] A hollow shell may be produced from the billet by performing another hot working method. For example, in a case where the steel material is a heavy-wall steel pipe of a short length such as a coupling, a hollow shell may be produced by forging by the Ehrhardt process or the like. A hollow shell is produced by the above process. Although not particularly limited, the wall thickness of the hollow shell is, for example, 9 to 60 mm.

[0120] If the steel material is a round steel bar, first, the starting material is heated in a heating furnace. Although not particularly limited, the heating temperature is, for example, 1100 to 1300°C. The starting material extracted from the heating furnace is subjected to hot working to produce an intermediate steel material in which a cross section perpendicular to the axial direction is a circular shape. The hot working is, for example, blooming performed using a blooming mill or hot rolling performed using a continuous mill. In a continuous mill, a horizontal stand having a pair of grooved rolls arranged one on the other in the vertical direction, and a vertical stand having a pair of grooved rolls arranged side by side in the horizontal direction are alternately arranged.

[0121] If the steel material is a steel plate, first, the starting material is heated in a heating furnace. Although not particularly limited, the heating temperature is, for example, 1100 to 1300°C. The starting material extracted from the heating furnace is subjected to hot rolling using a blooming mill and a continuous mill to produce an intermediate steel material having a steel plate shape.

[0122] The intermediate steel material produced by hot working may be air-cooled (as-rolled). The intermediate steel material produced by hot working may be subjected to direct quenching after hot working without being cooled to normal temperature, or may be subjected to quenching after undergoing supplementary heating (reheating) after hot working.

[0123] In a case of performing direct quenching after hot working, or performing quenching after supplementary heating, cooling may be stopped midway through the quenching process or slow cooling may be performed. In this case, the occurrence of quench cracking in the intermediate steel material can be suppressed. In addition, in the case of performing direct quenching after hot working, or performing quenching after supplementary heating, stress relief annealing (SR) may be performed at a time that is after quenching and before the heat treatment of the next process. In this case, residual stress of the intermediate steel material is eliminated. The heat treatment process is described in detail hereunder.

[Heat treatment process]

[0124] The heat treatment process includes a quenching process and a tempering process.

[Quenching process]

[0125] In the heat treatment process, first, the intermediate steel material produced in the hot working process is subjected to quenching (quenching process). The quenching is performed by a well-known method. Specifically, the intermediate steel material after the hot working process is charged into a heat treatment furnace and held at a quenching temperature. The quenching temperature is equal to or higher than the A_3 point, and for example is 900 to 1000°C. After being held at the quenching temperature, the intermediate steel material is rapidly cooled (quenched). Although not particularly limited, the holding time at the quenching temperature is, for example, 10 to 60 minutes. The quenching

method is, for example, water cooling. The quenching method is not particularly limited. In a case where the intermediate steel material is a hollow shell, for example, the hollow shell may be rapidly cooled by immersing the hollow shell in a water bath or an oil bath, or the hollow shell may be rapidly cooled by pouring or jetting cooling water onto the outer surface and/or inner surface of the hollow shell by shower cooling or mist cooling.

[0126] Note that, as mentioned above, after the hot working process, quenching (direct quenching) may be performed immediately after the hot working, without cooling the intermediate steel material to normal temperature, or quenching may be performed after the intermediate steel material has been held at the quenching temperature after being charged into a holding furnace before the temperature of the intermediate steel material decreased after the hot working.

[Tempering process]

[0127] The intermediate steel material after quenching is also subjected to a tempering process. In the tempering process, the yield strength of the steel material is adjusted. In the present embodiment, the tempering temperature is to be set in the range of 540 to 620°C. Although not particularly limited, the holding time (tempering time) at the tempering temperature is, for example, 10 to 180 minutes. Here, the term "tempering temperature" means the temperature of the heat treatment furnace in which tempering is carried out. Further, the term "tempering time" means the time period for which the intermediate steel material is held at the tempering temperature. Note that, it is well-known by those skilled in the art that the yield strength of a steel material can be adjusted by appropriately adjusting the tempering temperature according to the chemical composition. That is, in the present embodiment, the tempering conditions are adjusted so that the yield strength of the steel material becomes 862 MPa or more.

[0128] The martensitic stainless steel material according to the present embodiment can be produced by the process described above. Note that, as mentioned above, a method for producing the martensitic stainless steel material according to the present embodiment is not limited to the above production method. Specifically, as long as a martensitic stainless steel material which has the aforementioned chemical composition, satisfies Formula (1), has a yield strength of 862 MPa or more, and furthermore, in which the number ratio of coarse Mg oxides with respect to the specific inclusions is 45.0% or more can be produced, the production method of the present embodiment is not limited to the production method described above. Hereunder, the martensitic stainless steel material according to the present embodiment is described more specifically by way of examples.

EXAMPLE 1

[0129] Molten steels having the chemical compositions shown in Table 1-1 and Table 1-2 were produced. Note that, the symbol "-" in Table 1-2 means that the content of the corresponding element was at an impurity level. For example, it means that the contents of Cu, Nb and W of Test No. 1 were each 0% when rounded off to two decimal places. Further, it means that the contents of Zr of Test No. 1 were each 0% when rounded off to three decimal places. Furthermore, it means that the contents of B and REM of Test No. 1 were each 0% when rounded off to four decimal places. In addition, Fn1 and Fn2 that were determined based on the chemical composition of each test number listed in Table 1-1 and Table 1-2 and the definitions described above are shown in Table 2.

[Table 1-1]

[0130]

TABLE 1-1

Test Number	Chemical Composition (unit is mass%; balance is Fe and impurities)										
	C	Si	Mn	P	S	Cr	Ni	Mo	Co	Ti	V
1	0.012	0.23	0.42	0.010	0.0012	12.15	7.08	3.02	0.24	0.12	0.06
2	0.009	0.25	0.38	0.012	0.0008	12.05	7.12	2.96	0.22	0.11	0.05
3	0.010	0.24	0.41	0.015	0.0010	11.89	6.89	2.86	0.20	0.11	0.26
4	0.009	0.56	0.39	0.012	0.0010	12.15	6.82	2.88	0.13	0.11	0.05
5	0.010	0.25	0.58	0.013	0.0009	11.98	6.79	3.02	0.14	0.11	0.06
6	0.012	0.24	0.41	0.015	0.0009	13.15	6.38	3.10	0.15	0.11	0.05
7	0.012	0.28	0.38	0.015	0.0012	12.32	4.75	2.98	0.09	0.11	0.05
8	0.009	0.25	0.40	0.012	0.0011	11.78	6.94	3.89	0.16	0.11	0.06

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(continued)

	Test Number	Chemical Composition (unit is mass%; balance is Fe and impurities)										
		C	Si	Mn	P	S	Cr	Ni	Mo	Co	Ti	V
5	9	0.011	0.26	0.40	0.015	0.0015	11.85	7.13	2.88	0.21	0.22	0.06
	10	0.010	0.32	0.41	0.012	0.0010	11.88	6.98	2.89	0.19	0.11	0.54
	11	0.009	0.25	0.41	0.010	0.0012	12.24	6.32	2.32	0.21	0.11	0.06
10	12	0.011	0.28	0.40	0.014	0.0011	12.32	6.56	2.48	0.19	0.12	0.05
	13	0.013	0.32	0.42	0.016	0.0012	11.96	6.75	2.92	0.19	0.11	0.07
	14	0.011	0.28	0.41	0.008	0.0014	11.98	6.68	2.56	0.16	0.12	0.06
15	15	0.010	0.25	0.39	0.009	0.0009	12.08	6.28	2.78	0.11	0.10	0.05
	16	0.012	0.22	0.38	0.014	0.0008	12.35	6.32	2.48	0.21	0.12	0.05
	17	0.011	0.25	0.41	0.016	0.0018	12.07	7.08	2.91	0.21	0.09	0.08
20	18	0.010	0.18	0.39	0.015	0.0012	12.23	7.12	3.08	0.17	0.10	0.05
	19	0.009	0.25	0.38	0.013	0.0009	12.26	7.11	3.01	0.18	0.12	0.05
	20	0.012	0.23	0.41	0.018	0.0020	12.21	6.85	2.56	0.23	0.11	0.06
25	21	0.009	0.24	0.40	0.014	0.0018	12.16	6.98	2.88	0.22	0.10	0.06
	22	0.010	0.24	0.40	0.018	0.0008	11.79	6.86	2.98	0.05	0.11	0.06
	23	0.008	0.26	0.36	0.015	0.0013	11.76	6.92	2.78	0.19	0.12	0.05
30	24	0.009	0.22	0.38	0.014	0.0009	11.88	6.75	3.11	0.18	0.11	0.05
	25	0.010	0.27	0.41	0.016	0.0011	11.68	6.78	2.87	0.22	0.10	0.05
	26	0.012	0.23	0.42	0.010	0.0012	12.15	7.08	3.02	0.24	0.12	0.06
	27	0.010	0.30	0.40	0.015	0.0008	12.16	6.78	2.88	0.15	0.11	0.05

[Table 1-2]

35 **[0131]**

TABLE 1-2

Test Number	Chemical Composition (unit is mass%; balance is Fe and impurities)										
	Ca	Mg	Al	N	O	Cu	Nb	Zr	W	B	REM
40	1	0.0015	0.0007	0.021	0.0085	0.0026	-	-	-	-	-
	2	0.0021	0.0012	0.028	0.0105	0.0025	-	-	-	-	-
45	3	0.0026	0.0008	0.025	0.0092	0.0031	-	-	-	-	-
	4	0.0021	0.0015	0.030	0.0104	0.0021	-	-	-	-	-
	5	0.0020	0.0016	0.028	0.0098	0.0018	-	-	-	-	-
	6	0.0020	0.0012	0.031	0.0088	0.0023	-	-	-	-	-
50	7	0.0018	0.0008	0.031	0.0089	0.0021	-	-	-	-	-
	8	0.0024	0.0013	0.027	0.0076	0.0023	-	-	-	-	-
	9	0.0023	0.0012	0.027	0.0084	0.0017	-	-	-	-	-
55	10	0.0018	0.0018	0.028	0.0103	0.0021	-	-	-	-	-
	11	0.0024	0.0015	0.032	0.0068	0.0036	0.15	-	-	-	-
	12	0.0018	0.0022	0.028	0.0075	0.0018	-	0.10	-	-	-
	13	0.0019	0.0016	0.031	0.0095	0.0016	-	-	0.002	-	-

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(continued)

Test Number	Chemical Composition (unit is mass%; balance is Fe and impurities)										
	Ca	Mg	Al	N	O	Cu	Nb	Zr	W	B	REM
14	0.0025	0.0008	0.030	0.0096	0.0025	-	-	-	0.15	-	-
15	0.0022	0.0011	0.028	0.0102	0.0019	-	-	-	-	0.0020	-
16	0.0018	0.0012	0.024	0.0103	0.0024	-	-	-	-	-	0.0020
17	0.0012	0.0007	0.025	0.0096	0.0029	-	-	-	-	-	-
18	0.0008	0.0012	0.028	0.0082	0.0036	-	-	-	-	-	-
19	0.0018	0.0006	0.004	0.0078	0.0020	-	-	-	-	-	-
20	0.0045	0.0008	0.024	0.0071	0.0031	-	-	-	-	-	-
21	0.0031	0.0024	0.026	0.0088	0.0032	-	-	-	-	-	-
22	0.0001	0.0020	0.032	0.0130	0.0041	-	-	-	-	-	-
23	0.0002	0.0012	0.029	0.0075	0.0024	-	-	-	-	-	-
24	0.0018	0.0004	0.031	0.0077	0.0034	-	-	-	-	-	-
25	0.0002	0.0002	0.023	0.0082	0.0029	-	-	-	-	-	-
26	0.0015	0.0007	0.021	0.0085	0.0026	-	-	-	-	-	-
27	0.0025	0.0018	0.032	0.0092	0.0032	-	-	-	-	-	-

[Table 2]

[0132]

TABLE 2

Test Number	Fn1	Fn2	Order of Mg-Ca Addition	Holding Time			Tempering Temperature (°C)	Tempering Time (mins)
				tA (sec)	tB (sec)	FnC (tA/tB)		
1	0.0022	1.25	A	180	90	2.0	600	45
2	0.0033	2.63	A	180	90	2.0	600	30
3	0.0034	2.60	A	300	90	3.3	600	30
4	0.0036	2.10	A	300	60	5.0	600	45
5	0.0036	2.22	A	300	60	5.0	600	30
6	0.0032	2.22	A	300	60	5.0	600	30
7	0.0026	1.50	A	300	60	5.0	600	30
8	0.0037	2.18	A	300	60	5.0	600	45
9	0.0035	1.53	A	300	60	5.0	600	45
10	0.0036	1.80	A	300	60	5.0	600	30
11	0.0039	2.00	A	300	60	5.0	600	45
12	0.0040	1.64	A	300	60	5.0	600	45
13	0.0035	1.58	A	300	60	5.0	600	45
14	0.0033	1.79	A	300	60	5.0	600	45
15	0.0033	2.44	A	600	60	10.0	600	45
16	0.0030	2.25	A	300	60	5.0	600	45
17	0.0019	0.67	A	300	90	3.3	600	30

(continued)

Test Number	Fn1	Fn2	Order of Mg-Ca Addition	Holding Time			Tempering Temperature (°C)	Tempering Time (mins)
				tA (sec)	tB (sec)	FnC (tA/tB)		
18	0.0020	0.67	A	300	90	3.3	600	30
19	0.0024	2.00	A	180	300	0.6	600	30
20	0.0053	2.25	A	300	90	3.3	600	45
21	0.0055	1.72	A	300	90	3.3	600	30
22	0.0021	0.13	A	300	60	5.0	600	45
23	0.0014	0.15	A	300	60	5.0	600	30
24	0.0022	2.00	A	300	60	5.0	600	30
25	0.0004	0.18	A	300	90	3.3	600	30
26	0.0022	1.25	NA	300	90	3.3	600	30
27	0.0043	3.13	A	60	90	0.7	600	30

[0133] The molten steel of each test number was produced as follows. The molten steel containing Cr was placed in a ladle and a well-known rough decarburization refining process and Cr reduction treatment process were performed by the AOD process. After the Cr reduction treatment process, a slag removal treatment process in which slag was removed from the molten steel was performed. In addition, a well-known finishing decarburization refining process and Cr reduction treatment process were performed by the VOD process.

[0134] After the Cr reduction treatment process was performed by the VOD process, final composition adjustment of the molten steel in the ladle was performed by LT. At such time, molten steels to which Ca was added after Mg was added are described as "A (Acceptable)" in the column "Order of Mg-Ca Addition" in Table 2. On the other hand, a molten steel to which Mg was added after Ca was added is described as "NA (Not Acceptable)" in the column "Order of Mg-Ca Addition" in Table 2.

[0135] Further, in each test number other than Test No. 26, the holding time tA (secs) from when Mg was added and the uniform mixing time τ passed until Ca was added was adjusted as shown in Table 2. In addition, in each test number other than Test No. 26, the holding time tB (secs) from when Ca was added and the uniform mixing time τ passed until the molten steel was tapped was adjusted as shown in Table 2. Note that, with respect to Test No. 26, the time from when Ca was added and the uniform mixing time τ passed until Mg was added is shown as the holding time tA (secs) in Table 2. Further, with respect to Test No. 26, the time from when Mg was added and the uniform mixing time τ passed until the molten steel was tapped is shown as the holding time tB (secs) in Table 2. In addition, FnC (= tA/tB) that was determined based on the holding time tA (secs), the holding time tB (secs), and the aforementioned Formula (C) for each test number is shown in Table 2. Molten steels having the chemical compositions shown in Tables 1-1 and 1-2 were produced by the above process.

[0136] An ingot was produced by an ingot-making process from the produced molten steel of each test number. The ingot of each test number was heated for three hours at 1250°C. The ingot after heating was subjected to hot forging to produce a plurality of blocks for each of the respective test numbers. Hot rolling was performed on one block of each test number. Specifically, a block of each test number after hot forging was heated for three hours at 1230°C, and thereafter the block was subjected to hot rolling. In this way, a steel material (a steel plate) of each test number having a thickness of 13 mm was produced.

[0137] The produced steel material of each test number was subjected to quenching. Specifically, the steel plate of each test number was held at 910°C for 15 minutes, and thereafter subjected to water cooling. The steel plate of each test number after quenching was subjected to tempering in which the steel plate was held at a tempering temperature (°C) described in Table 2 for a tempering time (mins) described in Table 2. The steel plate of each test number was produced by the above production process.

[Evaluation Tests]

[0138] The produced steel plate of each test number was subjected to a tensile test, a number of specific inclusions measurement test, a hot workability test, and a corrosion resistance test.

[Tensile test]

[0139] The steel plate of each test number was subjected to a tensile test in accordance with ASTM E8/E8M (2021). Specifically, from a central position of the thickness of the steel plate of each test number, a round bar tensile test specimen in which the diameter of the parallel portion was made 8.9 mm, and the gage length was made 35.6 mm was prepared. The longitudinal direction of the round bar tensile test specimen was parallel to the rolling elongation direction of the steel plate. A tensile test was performed at normal temperature ($24 \pm 3^{\circ}\text{C}$) in the atmosphere using the round bar tensile test specimen of each test number, and the 0.2% offset proof stress (MPa) was determined. The determined 0.2% offset proof stress was defined as the yield strength (MPa). The obtained yield strength of each test number is shown in the column "YS (MPa)" in Table 3.

[Table 3]

[0140]

TABLE 3

Test Number	YS (MPa)	Ca (O, S) (/cm ²)	MgO (/cm ²)	Specific Inclusions (/cm ²)	MgO Ratio (%)	Ra (%)	Corrosion Resistance (150°C)
1	906	119	1141	1260	90.6	79	EX
2	912	321	958	1279	74.9	76	EX
3	905	356	712	1068	66.7	80	EX
4	945	346	1035	1381	74.9	72	EX
5	915	267	1023	1290	79.3	71	EX
6	912	369	864	1233	70.1	76	EX
7	938	310	768	1078	71.2	72	EX
8	978	465	886	1351	65.6	73	EX
9	980	328	880	1208	72.8	80	EX
10	908	263	863	1126	76.6	78	EX
11	889	617	1038	1655	62.7	76	EX
12	868	125	1215	1340	90.7	80	EX
13	898	546	1008	1554	64.9	75	EX
14	912	645	678	1323	51.2	72	EX
15	905	512	532	1044	51.0	71	EX
16	917	265	952	1217	78.2	72	EX
17	896	228	612	840	49.4	66	EX
18	876	332	615	947	54.4	67	EX
19	910	48	82	130	63.1	58	EX
20	907	1548	37	1585	2.3	78	NA
21	901	1315	965	2280	42.3	76	NA
22	915	6	933	939	99.4	69	EX
23	895	18	612	630	97.1	66	EX
24	925	1215	24	1239	1.9	75	NA
25	883	30	86	116	74.1	65	EX
26	908	1156	135	1291	10.5	78	NA
27	885	1056	28	1084	2.6	72	NA

[Number of specific inclusions measurement test]

[0141] Using the method described above, the total number density (/cm²) of Ca oxides having an equivalent circular diameter of 2.0 μm or more (coarse Ca oxides) and Ca sulfides having an equivalent circular diameter of 2.0 μm or more (coarse Ca sulfides), and the number density (/cm²) of Mg oxides having an equivalent circular diameter of 2.0 μm or more (coarse Mg oxides) were determined for the steel plate of each test number. The obtained total number density of coarse Ca oxides and coarse Ca sulfides of each test number is shown in the column "Ca (O, S) (/cm²)" in Table 3. In addition, the obtained number density of coarse Mg oxides of each test number is shown in the column "MgO (/cm²)" in Table 3. Further, the total number density of coarse Ca oxides, coarse Ca sulfides, and coarse Mg oxides of each test number is shown in the column "Specific Inclusions (/cm²)" in Table 3. In addition, the number ratio of coarse Mg oxides with respect to the specific inclusions in each test number is shown in the column "MgO Ratio (%)" in Table 3.

[Hot workability test]

[0142] A block of each test number was subjected to a hot workability test (Gleeble test) by the method described above. Note that, as mentioned above, the term "a block of each test number" refers to a block obtained by performing hot forging on an ingot produced from the molten steel of each test number. A round bar specimen was prepared from the block of each test number. Specifically, for the block of each test number, the direction in which hot rolling was performed (corresponds to the rolling elongation direction of the produced steel plate) was identified. In addition, among the surfaces of the block of each test number, the surface on which hot rolling was performed (surface perpendicular to the thickness direction of the steel plate) was identified. From the block of each test number, a round bar specimen was prepared from the center position between the surface on which hot rolling was performed and a point of intersection of two diagonal lines in a cross section perpendicular to the direction in which hot rolling was performed (rolling elongation direction of the steel plate).

[0143] Each round bar specimen was prepared so as to be 10 mm in diameter and 130 mm in length. The longitudinal direction of the round bar specimen was made parallel to the direction in which hot rolling was performed on the block (rolling elongation direction of the steel plate). After heating the round bar specimen of each test number to 900°C, a tensile test was carried out at a strain rate of 10s⁻¹ to cause the round bar specimen of each test number to break. A reduction value Ra (%) was determined based on the broken round bar specimen of each test number. The obtained reduction value Ra of each test number is shown in the column "Ra (%)" in Table 3.

[Corrosion resistance test]

[0144] The steel plate of each test number was subjected to a corrosion resistance test (corrosion rate test) by the method described above. Specifically, a test specimen having a length of 30 mm, a width of 20 mm, and a thickness of 2 mm was prepared from a central position of the thickness of the steel plate of each test number. Note that, the longitudinal direction of the test specimen was made parallel to the rolling elongation direction. The test specimen of each test number was immersed in an aqueous solution containing 5.0% sodium chloride by mass inside an autoclave. A gaseous mixture (SO₂, NO₂, and CO₂) at a total pressure of 130 bar having an SO₂ concentration of 10 ppm and an NO₂ concentration of 10 ppm was sealed under pressure inside the autoclave. The temperature inside the autoclave was maintained at 150°C, and the corrosion rate test was performed for 96 hours.

[0145] The corrosion rate (mm/year) of each test specimen after the 96 hours elapsed was determined based on the mass, density, and surface area. In addition, each test specimen after the 96 hours elapsed was observed using a magnifying glass with a magnification of ×10 and an optical microscope with a magnification of ×100, and the presence or absence of pitting was confirmed. If the obtained corrosion rate was 0.100 mm/year or less and pitting was not confirmed, it was determined that the relevant test specimen had excellent corrosion resistance in a corrosive environment in which SOx or NOx is mixed ("EX (Excellent)" in the column "Corrosion Resistance (150°C)" in Table 3). On the other hand, if the obtained corrosion rate was more than 0.100 mm/year or if pitting was confirmed, it was determined that the relevant test specimen did not have excellent corrosion resistance in a corrosive environment in which SOx or NOx is mixed ("NA (Not Acceptable)" in the column "Corrosion Resistance (150°C)" in Table 3). The evaluation of corrosion resistance for each test number is shown in Table 3.

[Evaluation results]

[0146] Referring to Tables 1-1, 1-2, 2 and 3, with respect to the steel plates of Test Nos. 1 to 19, the chemical composition was appropriate and Fn1 was in the range of 0.0010 to 0.0050. These steel plates also had a yield strength of 862 MPa or more. Further, in these steel plates, the number ratio of coarse Mg oxides with respect to the specific inclusions was 45.0% or more. As a result, in the corrosion resistance test, these steel plates had excellent corrosion resistance in a corrosive environment in which SOx or NOx was mixed. Note that, based on these evaluation results, it was determined that these

steel plates had a microstructure composed of, in volume ratio, 0 to 5% of retained austenite and 0 to 5% of ferrite, with the balance being martensite.

[0147] Furthermore, in the steel plates of Test Nos. 1 to 16, Fn2 was 0.80 or more, and the production method was a preferable production method described above. As a result, in these steel plates, the total number density of the specific inclusions was 1000 /cm² or more. As a result, the reduction value Ra of these steel plates in the hot workability test was 70% or more, and thus these steel plates exhibited more excellent hot workability.

[0148] On the other hand, in the steel plates of Test No. 20 and 21, Fn1 was too high. As a result, in these steel plates, the number ratio of coarse Mg oxides to the specific inclusions was less than 45.0%. As a result, in the corrosion resistance test, these steel plates did not exhibit excellent corrosion resistance in a corrosive environment in which SOx or NOx was mixed.

[0149] In the steel plates of Test No. 22 and 23, the content of Ca was too low.

[0150] In the steel plate of Test No. 24, the content of Mg was too low. As a result, in this steel plate, the number ratio of coarse Mg oxides to the specific inclusions was less than 45.0%. As a result, in the corrosion resistance test, this steel plate did not exhibit excellent corrosion resistance in a corrosive environment in which SOx or NOx was mixed.

[0151] In the steel plate of Test No. 25, the content of Ca was too low, the content of Mg was too low, and Fn1 was too low.

[0152] With respect to the steel plate of Test No. 26, during production of the molten steel, Mg was added after Ca was added. As a result, in this steel plate, the number ratio of coarse Mg oxides to the specific inclusions was less than 45.0%. As a result, in the corrosion resistance test, this steel plate did not exhibit excellent corrosion resistance in a corrosive environment in which SOx or NOx was mixed.

[0153] With respect to the steel plate of Test No. 27, during production of the molten steel, FnC was too small. As a result, in this steel plate, the number ratio of coarse Mg oxides to the specific inclusions was less than 45.0%. As a result, in the corrosion resistance test, this steel plate did not exhibit excellent corrosion resistance in a corrosive environment in which SOx or NOx was mixed.

EXAMPLE 2

[0154] In Example 2, advantageous effects of the martensitic stainless steel material according to the present embodiment in which the content of Cu is 0.50% or more and the content of W is 0.01% or more was confirmed. Specifically, molten steels having the chemical compositions shown in Table 4-1 and Table 4-2 were produced. Note that, the symbol "-" in Table 4-2 means that the content of the corresponding element was at an impurity level. For example, it means that the contents of Nb of Test No. 1 were each 0% when rounded off to two decimal places. Further, it means that the contents of Zr of Test No. 1 were each 0% when rounded off to three decimal places. Furthermore, it means that the contents of B and REM of Test No. 1 were each 0% when rounded off to four decimal places. In addition, Fn1 and Fn2 that were determined based on the chemical composition of each test number listed in Table 4-1 and Table 4-2 and the definitions described above are shown in Table 5.

[Table 4-1]

[0155]

TABLE 4-1

Test Number	Chemical Composition (unit is mass%; balance is Fe and impurities)										
	C	Si	Mn	P	S	Cr	Ni	Mo	Co	Ti	V
28	0.009	0.22	0.41	0.018	0.0010	12.75	6.19	2.65	0.21	0.12	0.05
29	0.014	0.25	0.39	0.014	0.0008	13.24	5.24	3.21	0.16	0.12	0.04
30	0.010	0.25	0.41	0.013	0.0012	12.65	5.46	2.63	0.18	0.11	0.04
31	0.012	0.68	0.40	0.014	0.0015	12.18	5.98	2.53	0.15	0.11	0.06
32	0.010	0.32	0.72	0.015	0.0004	13.48	5.86	3.12	0.14	0.12	0.05
33	0.009	0.28	0.46	0.012	0.0008	12.43	6.21	2.46	0.18	0.13	0.05
34	0.011	0.25	0.38	0.015	0.0010	11.28	5.24	2.64	0.08	0.15	0.05
35	0.010	0.24	0.40	0.012	0.0014	12.56	6.73	1.89	0.38	0.11	0.06
36	0.010	0.25	0.35	0.014	0.0008	12.68	6.15	3.62	0.23	0.10	0.04
37	0.012	0.26	0.36	0.010	0.0009	11.69	6.24	1.52	0.21	0.12	0.05

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(continued)

	Test Number	Chemical Composition (unit is mass%; balance is Fe and impurities)										
		C	Si	Mn	P	S	Cr	Ni	Mo	Co	Ti	V
5	38	0.009	0.27	0.40	0.013	0.0011	12.34	6.42	2.06	0.26	0.12	0.58
	39	0.012	0.25	0.45	0.015	0.0008	13.12	6.15	2.72	0.20	0.13	0.05
	40	0.012	0.22	0.38	0.014	0.0009	13.58	6.05	2.56	0.18	0.11	0.05
10	41	0.011	0.27	0.42	0.010	0.0009	13.54	5.76	2.51	0.16	0.10	0.06
	42	0.009	0.24	0.38	0.015	0.0010	12.86	6.15	2.61	0.15	0.11	0.05
	43	0.012	0.24	0.45	0.016	0.0012	13.18	6.08	1.89	0.23	0.11	0.05
15	44	0.009	0.25	0.38	0.017	0.0008	13.35	6.13	2.72	0.26	0.11	0.05
	45	0.010	0.24	0.41	0.013	0.0006	13.12	5.52	2.86	0.15	0.11	0.05
	46	0.013	0.25	0.41	0.015	0.0005	12.86	6.18	2.61	0.18	0.12	0.04
20	47	0.015	0.28	0.44	0.015	0.0010	13.16	5.46	1.63	0.16	0.11	0.06
	48	0.012	0.25	0.42	0.012	0.0030	12.95	5.64	2.15	0.31	0.12	0.04
	49	0.009	0.23	0.41	0.018	0.0015	12.69	6.27	2.65	0.21	0.13	0.05
25	50	0.009	0.22	0.41	0.018	0.0015	12.69	6.24	2.64	0.21	0.12	0.05
	51	0.013	0.22	0.40	0.012	0.0020	13.25	5.25	1.67	0.17	0.11	0.04
	52	0.011	0.24	0.41	0.015	0.0008	12.82	6.23	2.62	0.16	0.12	0.05
30	53	0.011	0.24	0.38	0.012	0.0012	12.86	6.21	2.52	0.20	0.11	0.12
	54	0.010	0.32	0.45	0.015	0.0018	10.86	5.26	2.46	0.12	0.12	0.06
	55	0.011	0.28	0.38	0.012	0.0016	12.15	3.86	2.14	0.06	0.13	0.05
	56	0.013	0.24	0.41	0.012	0.0023	12.69	6.23	1.37	0.18	0.09	0.04
	57	0.012	0.26	0.38	0.016	0.0011	12.86	6.06	2.56	0.18	0.11	0.05

[Table 4-2]

[0156]

TABLE 4-2

40	Test Number	Chemical Composition (unit is mass%; balance is Fe and impurities)										
		Ca	Mg	Al	N	O	Cu	Nb	Zr	W	B	REM
45	28	0.0010	0.0021	0.011	0.0077	0.0052	2.10	-	-	0.20	-	-
	29	0.0015	0.0013	0.030	0.0092	0.0028	1.56	-	-	0.35	-	-
	30	0.0018	0.0015	0.028	0.0075	0.0022	2.58	-	-	0.12	-	-
	31	0.0018	0.0008	0.030	0.0083	0.0026	2.13	-	-	0.21	-	-
	32	0.0032	0.0014	0.031	0.0075	0.0031	2.32	-	-	0.14	-	-
50	33	0.0025	0.0007	0.035	0.0088	0.0028	0.86	-	-	0.21	-	-
	34	0.0014	0.0009	0.028	0.0096	0.0035	1.86	-	-	0.32	-	-
	35	0.0024	0.0012	0.026	0.0105	0.0016	2.12	-	-	0.42	-	-
55	36	0.0038	0.0006	0.031	0.0095	0.0018	1.93	-	-	0.10	-	-
	37	0.0026	0.0010	0.027	0.0106	0.0038	2.35	-	-	1.54	-	-
	38	0.0013	0.0018	0.029	0.0124	0.0031	2.31	-	-	0.46	-	-
	39	0.0007	0.0015	0.038	0.0103	0.0031	1.68	0.05	-	0.13	-	-

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(continued)

	Test Number	Chemical Composition (unit is mass%; balance is Fe and impurities)										
		Ca	Mg	Al	N	O	Cu	Nb	Zr	W	B	REM
5	40	0.0012	0.0009	0.032	0.0085	0.0028	1.72	-	-	0.18	0.0030	-
	41	0.0008	0.0017	0.023	0.0078	0.0042	1.82	-	-	0.15	-	0.0020
	42	0.0015	0.0014	0.030	0.0102	0.0026	1.92	-	0.002	0.28	-	-
10	43	0.0007	0.0010	0.032	0.0092	0.0031	2.18	-	-	0.25	-	-
	44	0.0006	0.0008	0.032	0.0088	0.0035	2.31	-	-	0.21	-	-
	45	0.0012	0.0008	0.028	0.0085	0.0021	2.15	-	-	0.02	-	-
15	46	0.0003	0.0012	0.028	0.0085	0.0028	1.98	-	-	0.23	-	-
	47	0.0045	0.0012	0.021	0.0080	0.0035	2.38	-	-	0.15	-	-
	48	0.0035	0.0018	0.030	0.0115	0.0030	2.35	-	-	0.12	-	-
20	49	0.0032	0.0001	0.031	0.0087	0.0046	2.12	-	-	0.21	-	-
	50	0.0001	0.0001	0.024	0.0080	0.0027	2.10	-	-	0.20	-	-
	51	0.0003	0.0004	0.031	0.0085	0.0030	1.48	-	-	0.25	-	-
25	52	0.0025	0.0016	0.035	0.0086	0.0036	2.06	-	-	0.22	-	-
	53	0.0024	0.0012	0.033	0.0086	0.0036	3.68	-	-	0.20	-	-
	54	0.0025	0.0007	0.032	0.0084	0.0046	1.96	-	-	0.23	-	-
30	55	0.0018	0.0008	0.019	0.0089	0.0032	2.37	-	-	0.36	-	-
	56	0.0023	0.0012	0.020	0.0094	0.0048	1.89	-	-	0.26	-	-
	57	0.0018	0.0025	0.026	0.0078	0.0032	2.32	-	-	0.18	-	-

[Table 5]

[0157]

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TABLE 5

40	Test Number	Fn1	Fn2	Order of Mg-Ca Addition	Holding Time			Tempering Temperature (°C)	Tempering Time (mins)
					tA (sec)	tB (sec)	FnC (tA/tB)		
45	28	0.0031	1.00	A	180	90	2.0	610	45
	29	0.0028	1.88	A	180	90	2.0	610	45
	30	0.0033	1.50	A	300	90	3.3	610	45
	31	0.0026	1.20	A	300	60	5.0	600	30
	32	0.0046	8.00	A	300	60	5.0	600	30
50	33	0.0032	3.13	A	300	60	5.0	580	30
	34	0.0023	1.40	A	300	60	5.0	600	30
	35	0.0036	1.71	A	300	60	5.0	600	30
	36	0.0044	4.75	A	600	60	10.0	600	30
	37	0.0036	2.89	A	180	90	2.0	600	30
55	38	0.0031	1.18	A	180	90	2.0	600	30
	39	0.0022	0.88	A	180	90	2.0	600	30
	40	0.0021	1.33	A	180	90	2.0	600	30

(continued)

Test Number	Fn1	Fn2	Order of Mg-Ca Addition	Holding Time			Tempering Temperature (°C)	Tempering Time (mins)
				tA (sec)	tB (sec)	FnC (tA/tB)		
41	0.0025	0.89	A	180	90	2.0	600	30
42	0.0029	1.50	A	180	90	2.0	600	30
43	0.0017	0.58	A	180	90	2.0	610	45
44	0.0014	0.75	A	180	90	2.0	610	45
45	0.0020	2.00	A	180	300	0.6	600	30
46	0.0015	0.60	A	180	90	2.0	600	30
47	0.0057	4.50	A	180	60	3.0	610	45
48	0.0053	1.17	A	180	60	3.0	600	30
49	0.0033	2.13	A	300	60	5.0	610	45
50	0.0002	0.07	A	300	60	5.0	610	45
51	0.0007	0.15	A	300	60	5.0	610	45
52	0.0041	3.13	NA	180	60	3.0	610	45
53	0.0036	2.00	A	180	60	3.0	620	45
54	0.0032	1.39	A	180	60	3.0	600	30
55	0.0026	1.13	A	180	60	3.0	600	30
56	0.0035	1.00	A	180	60	3.0	600	30
57	0.0043	1.64	A	60	90	0.7	600	30

[0158] In a similar manner to Example 1, the molten steel of each test number was produced as follows. The molten steel containing Cr was placed in a ladle and a well-known rough decarburization refining process and Cr reduction treatment process were performed by the AOD process. After the Cr reduction treatment process, a slag removal treatment process in which slag was removed from the molten steel was performed. In addition, a well-known finishing decarburization refining process and Cr reduction treatment process were performed by the VOD process.

[0159] In a similar manner to Example 1, after the Cr reduction treatment process was performed by the VOD process, final composition adjustment of the molten steel in the ladle was performed by LT. At such time, molten steels to which Ca was added after Mg was added are described as "A" in the column "Order of Mg-Ca Addition" in Table 5. On the other hand, a molten steel to which Mg was added after Ca was added is described as "NA" in the column "Order of Mg-Ca Addition" in Table 5.

[0160] Further, in each test number other than Test No. 52, the holding time tA (secs) from when Mg was added and the uniform mixing time τ passed until Ca was added was adjusted as shown in Table 5. In addition, in each test number other than Test No. 52, the holding time tB (secs) from when Ca was added and the uniform mixing time τ passed until the molten steel was tapped was adjusted as shown in Table 5. Note that, with respect to Test No. 52, the time from when Ca was added and the uniform mixing time τ passed until Mg was added is shown as the holding time tA (secs) in Table 5. Further, with respect to Test No. 52, the time from when Mg was added and the uniform mixing time τ passed until the molten steel was tapped is shown as the holding time tB (secs) in Table 5. In addition, FnC (= tA/tB) that was determined based on the holding time tA (secs), the holding time tB (secs), and the aforementioned Formula (C) for each test number is shown in Table 5. Molten steels having the chemical compositions shown in Tables 4-1 and 4-2 were produced by the above process.

[0161] In a similar manner to Example 1, an ingot was produced by an ingot-making process from the produced molten steel of each test number. The ingot of each test number was heated for three hours at 1250°C. The ingot after heating was subjected to hot forging to produce a plurality of blocks for each of the respective test numbers. Hot rolling was performed on one block of each test number. Specifically, a block of each test number after hot forging was heated for three hours at 1230°C, and thereafter the block was subjected to hot rolling. In this way, a steel material (a steel plate) of each test number having a thickness of 13 mm was produced.

[0162] In a similar manner to Example 1, the produced steel material of each test number was subjected to quenching. Specifically, the steel plate of each test number was held at 910°C for 15 minutes, and thereafter subjected to water

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cooling. The steel plate of each test number after quenching was subjected to tempering in which the steel plate was held at a tempering temperature (°C) described in Table 5 for a tempering time (mins) described in Table 5. The steel plate of each test number was produced by the above production process.

5 [Evaluation Tests]

[0163] The produced steel plate of each test number was subjected to a tensile test, a number of specific inclusions measurement test, a hot workability test, and a corrosion resistance test.

10 [Tensile test]

[0164] The steel plate of each test number was subjected to a tensile test in accordance with ASTM E8/E8M (2021). Specifically, from a central position of the thickness of the steel plate of each test number, a round bar tensile test specimen in which the diameter of the parallel portion was made 8.9 mm, and the gage length was made 35.6 mm was prepared. The longitudinal direction of the round bar tensile test specimen was parallel to the rolling elongation direction of the steel plate. A tensile test was performed at normal temperature ($24 \pm 3^{\circ}\text{C}$) in the atmosphere using the round bar tensile test specimen of each test number, and the 0.2% offset proof stress (MPa) was determined. The determined 0.2% offset proof stress was defined as the yield strength (MPa). The obtained yield strength of each test number is shown in the column "YS (MPa)" in Table 6.

20 [Table 6]

[0165]

TABLE 6

Test Number	YS (MPa)	Ca (O, S) (/cm ²)	MgO (/cm ²)	Specific Inclusions (/cm ²)	MgO Ratio (%)	Ra (%)	Corrosion Resistance (175°C)
28	923	230	1894	2124	89.2	77	EX
29	886	952	1131	2083	54.3	76	EX
30	986	995	968	1963	49.3	77	EX
31	895	988	1230	2218	55.5	74	EX
32	883	878	965	1843	52.4	73	EX
33	866	868	815	1683	48.4	73	EX
34	896	310	868	1178	73.7	72	EX
35	887	965	845	1810	46.7	76	EX
36	932	586	594	1180	50.3	72	EX
37	912	968	945	1913	49.4	78	EX
38	994	243	813	1056	77.0	71	EX
39	892	114	1856	1970	94.2	74	EX
40	912	248	873	1121	77.9	73	EX
41	935	95	1109	1204	92.1	75	EX
42	904	930	1014	1944	52.2	75	EX
43	894	215	678	883	76.8	68	EX
44	918	186	716	902	79.4	69	EX
45	905	56	52	108	48.1	60	EX
46	938	58	826	884	93.4	65	EX
47	931	1915	913	2828	32.3	79	NA
48	904	1335	1048	2383	44.0	76	NA

(continued)

Test Number	YS (MPa)	Ca (O, S) (/cm ²)	MgO (/cm ²)	Specific Inclusions (/cm ²)	MgO Ratio (%)	Ra (%)	Corrosion Resistance (175°C)
49	925	1726	42	1768	2.4	82	NA
50	912	12	54	66	81.8	63	EX
51	869	97	602	699	86.1	69	EX
52	923	2128	27	2155	1.3	78	NA
53	1002	465	796	1261	63.1	58	EX
54	872	748	1200	1948	61.6	75	NA
55	896	321	814	1135	71.7	62	EX
56	869	948	1035	1983	52.2	74	NA
57	912	1032	56	1088	5.1	76	NA

[Number of specific inclusions measurement test]

[0166] Using the method described above, the total number density (/cm²) of Ca oxides having an equivalent circular diameter of 2.0 μm or more (coarse Ca oxides) and Ca sulfides having an equivalent circular diameter of 2.0 μm or more (coarse Ca sulfides), and the number density (/cm²) of Mg oxides having an equivalent circular diameter of 2.0 μm or more (coarse Mg oxides) were determined for the steel plate of each test number. The obtained total number density of coarse Ca oxides and coarse Ca sulfides of each test number is shown in the column "Ca (O, S) (/cm²)" in Table 6. In addition, the obtained number density of coarse Mg oxides of each test number is shown in the column "MgO (/cm²)" in Table 6. Further, the total number density of coarse Ca oxides, coarse Ca sulfides, and coarse Mg oxides of each test number is shown in the column "Specific Inclusions (/cm²)" in Table 6. In addition, the number ratio of coarse Mg oxides with respect to the specific inclusions in each test number is shown in the column "MgO Ratio (%)" in Table 6.

[Hot workability test]

[0167] A block of each test number was subjected to a hot workability test (Gleeble test) by the method described above. Note that, as mentioned above, the term "a block of each test number" refers to a block obtained by performing hot forging on an ingot produced from the molten steel of each test number. A round bar specimen was prepared from the block of each test number. Specifically, for the block of each test number, the direction in which hot rolling was performed (corresponds to the rolling elongation direction of the produced steel plate) was identified. In addition, among the surfaces of the block of each test number, the surface on which hot rolling was performed (surface perpendicular to the thickness direction of the steel plate) was identified. From the block of each test number, a round bar specimen was prepared from the center position between the surface on which hot rolling was performed and a point of intersection of two diagonal lines in a cross section perpendicular to the direction in which hot rolling was performed (rolling elongation direction of the steel plate).

[0168] Each round bar specimen was prepared so as to be 10 mm in diameter and 130 mm in length. The longitudinal direction of the round bar specimen was made parallel to the direction in which hot rolling was performed on the block (rolling elongation direction of the steel plate). After heating the round bar specimen of each test number to 900°C, a tensile test was carried out at a strain rate of 10s⁻¹ to cause the round bar specimen of each test number to break. A reduction value Ra (%) was determined based on the broken round bar specimen of each test number. The obtained reduction value Ra of each test number is shown in the column "Ra (%)" in Table 6.

[Corrosion resistance test]

[0169] The steel plate of each test number was subjected to a corrosion resistance test (corrosion rate test) by the method described above. Specifically, a test specimen having a length of 30 mm, a width of 20 mm, and a thickness of 2 mm was prepared from a central position of the thickness of the steel plate of each test number. Note that, the longitudinal direction of the test specimen was made parallel to the rolling elongation direction. The test specimen of each test number was immersed in an aqueous solution containing 5.0% sodium chloride by mass inside an autoclave. A gaseous mixture (SO₂, NO₂, and CO₂) at a total pressure of 130 bar having an SO₂ concentration of 10 ppm and an NO₂ concentration of 10 ppm was sealed under pressure inside the autoclave. The temperature inside the autoclave was maintained at 175°C, and

the corrosion rate test was performed for 96 hours.

[0170] The corrosion rate (mm/year) of each test specimen after the 96 hours elapsed was determined based on the mass, density, and surface area. In addition, each test specimen after the 96 hours elapsed was observed using a magnifying glass with a magnification of $\times 10$ and an optical microscope with a magnification of $\times 100$, and the presence or absence of pitting was confirmed. If the obtained corrosion rate was 0.100 mm/year or less and pitting was not confirmed, it was determined that the relevant test specimen had more excellent corrosion resistance in a corrosive environment in which SO_x or NO_x is mixed ("EX" in the column "Corrosion Resistance (175°C)" in Table 6). On the other hand, if the obtained corrosion rate was more than 0.100 mm/year or if pitting was confirmed, it was determined that the relevant test specimen did not have more excellent corrosion resistance in a corrosive environment in which SO_x or NO_x is mixed ("NA" in the column "Corrosion Resistance (175°C)" in Table 6). The evaluation of corrosion resistance for each test number is shown in Table 6.

[Evaluation results]

[0171] Referring to Tables 4-1, 4-2, 5 and 6, with respect to the steel plates of Test Nos. 28 to 45, the chemical composition was appropriate and Fn1 was in the range of 0.0010 to 0.0050. These steel plates also had a yield strength of 862 MPa or more. Further, in these steel plates, the number ratio of coarse Mg oxides with respect to the specific inclusions was 45.0% or more. As a result, in the corrosion resistance test, these steel plates had more excellent corrosion resistance in a corrosive environment in which SO_x or NO_x was mixed. Note that, based on these evaluation results, it was determined that these steel plates had a microstructure composed of, in volume ratio, 0 to 5% of retained austenite and 0 to 5% of ferrite, with the balance being martensite.

[0172] Furthermore, in the steel plates of Test Nos. 28 to 42, Fn2 was 0.80 or more, and the production method was a preferable production method described above. As a result, in these steel plates, the total number density of the specific inclusions was 1000 /cm² or more. As a result, the reduction value Ra of these steel plates in the hot workability test was 70% or more, and thus these steel plates exhibited more excellent hot workability.

[0173] On the other hand, in the steel plate of Test No. 46, the content of Ca was too low.

[0174] In the steel plates of Test No. 47 and 48, Fn1 was too high. As a result, in these steel plates, the number ratio of coarse Mg oxides to the specific inclusions was less than 45.0%. As a result, in the corrosion resistance test, these steel plates did not exhibit more excellent corrosion resistance in a corrosive environment in which SO_x or NO_x was mixed.

[0175] In the steel plate of Test No. 49, the content of Mg was too low. As a result, in this steel plate, the number ratio of coarse Mg oxides to the specific inclusions was less than 45.0%. As a result, in the corrosion resistance test, this steel plate did not exhibit more excellent corrosion resistance in a corrosive environment in which SO_x or NO_x was mixed.

[0176] In the steel plates of Test No. 50 and 51, the content of Ca was too low, the content of Mg was too low, and Fn1 was too low.

[0177] With respect to the steel plate of Test No. 52, during production of the molten steel, Mg was added after Ca was added. As a result, in this steel plate, the number ratio of coarse Mg oxides to the specific inclusions was less than 45.0%. As a result, in the corrosion resistance test, this steel plate did not exhibit more excellent corrosion resistance in a corrosive environment in which SO_x or NO_x was mixed.

[0178] In the steel plate of Test No. 53, the content of Cu was too high.

[0179] In the steel plate of Test No. 54, the content of Cr was too low. As a result, in the corrosion resistance test, this steel plate did not exhibit more excellent corrosion resistance in a corrosive environment in which SO_x or NO_x was mixed.

[0180] In the steel plate of Test No. 55, the content of Ni was too low.

[0181] In the steel plate of Test No. 56, the content of Mo was too low. As a result, in the corrosion resistance test, this steel plate did not exhibit more excellent corrosion resistance in a corrosive environment in which SO_x or NO_x was mixed.

[0182] With respect to the steel plate of Test No. 57, during production of the molten steel, FnC was too small. As a result, in this steel plate, the number ratio of coarse Mg oxides to the specific inclusions was less than 45.0%. As a result, in the corrosion resistance test, this steel plate did not exhibit more excellent corrosion resistance in a corrosive environment in which SO_x or NO_x was mixed.

[0183] An embodiment of the present disclosure has been described above. However, the embodiment described above is merely an example for carrying out the present disclosure. Therefore, the present disclosure is not limited to the above-described embodiment, and can be implemented by appropriately modifying the above-described embodiment within a range not departing from the spirit thereof.

Claims

1. A martensitic stainless steel material consisting of, in mass%,

C: 0.030% or less,
 Si: 1.00% or less,
 Mn: 1.00% or less,
 P: 0.030% or less,
 S: 0.0050% or less,
 Cr: 11.00 to 14.00%,
 Ni: 4.00 to 7.50%,
 Mo: 1.50 to 4.50%,
 Co: 0.01 to 0.50%,
 Ti: 0.05 to 0.30%,
 V: 0.01 to 1.00%,
 Ca: 0.0005 to 0.0050%,
 Mg: 0.0005 to 0.0050%,
 Al: 0.001 to 0.100%,
 N: 0.0500% or less,
 O: 0.0500% or less,
 Cu: 0 to 3.50%,
 Nb: 0 to 0.50%,
 Zr: 0 to 0.050%,
 W: 0 to 2.00%,
 B: 0 to 0.0050%,
 rare earth metal: 0 to 0.0050%, and
 the balance: Fe and impurities,
 wherein:

within ranges of contents of elements of the martensitic stainless steel material, contents of the elements satisfy Formula (1);
 a yield strength is 862 MPa or more; and
 in the martensitic stainless steel material,
 a number ratio of Mg oxides having an equivalent circular diameter of 2.0 μm or more with respect to Ca oxides having an equivalent circular diameter of 2.0 μm or more, Ca sulfides having an equivalent circular diameter of 2.0 μm or more, and the Mg oxides having an equivalent circular diameter of 2.0 μm or more is 45.0% or more;

$$0.0010 \leq \text{Ca} + \text{Mg} \leq 0.0050 \dots (1)$$

where, a content of a corresponding element in percent by mass is substituted for each symbol of an element in Formula (1).

2. The martensitic stainless steel material according to claim 1, containing one or more elements selected from a group consisting of:

Cu: 0.01 to 3.50%,
 Nb: 0.01 to 0.50%,
 Zr: 0.001 to 0.050%,
 W: 0.01 to 2.00%,
 B: 0.0001 to 0.0050%, and
 rare earth metal: 0.0001 to 0.0050%.

3. The martensitic stainless steel material according to claim 1 or claim 2, wherein:

within ranges of contents of elements of the martensitic stainless steel material, contents of the elements satisfy Formula (2); and
 in the martensitic stainless steel material,
 a total number density of the Ca oxides having an equivalent circular diameter of 2.0 μm or more, the Ca sulfides having an equivalent circular diameter of 2.0 μm or more, and the Mg oxides having an equivalent circular diameter of 2.0 μm or more is 1000 / cm^2 or more;

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$$\text{Ca/S} \geq 0.80 \dots (2)$$

where, a content of a corresponding element in percent by mass is substituted for each symbol of an element in Formula (2).

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2023/017933

A. CLASSIFICATION OF SUBJECT MATTER

C22C 38/00(2006.01)i; **B21B 1/16**(2006.01)i; **B21B 1/22**(2006.01)i; **B21B 3/00**(2006.01)i; **B21B 19/04**(2006.01)i;
B21B 19/10(2006.01)i; **C21C 7/00**(2006.01)i; **C21D 6/00**(2006.01)i; **C21D 8/00**(2006.01)i; **C21D 9/08**(2006.01)i;
C22C 38/54(2006.01)i

FI: C22C38/00 302Z; C22C38/54; B21B1/16 B; B21B1/22 M; B21B19/04; B21B19/10; C21D8/00 E; C21D6/00 102J;
C21D9/08 E; C21C7/00 A; C21C7/00 B; B21B3/00 D

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B21B3/00; B21B19/04; B21B19/10; C21C7/00; C21D6/00; C21D8/00; C21D9/08; C22C38/00; C22C38/54; B21B1/16;
B21B1/22

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2023
Registered utility model specifications of Japan 1996-2023
Published registered utility model applications of Japan 1994-2023

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2022/075405 A1 (NIPPON STEEL CORP.) 14 April 2022 (2022-04-14)	1-3
A	WO 2022/075406 A1 (NIPPON STEEL CORP.) 14 April 2022 (2022-04-14)	1-3
A	JP 2018-35381 A (NIPPON STEEL & SUMITOMO METAL CORP.) 08 March 2018 (2018-03-08)	1-3
A	JP 2019-143228 A (NIPPON STEEL STAINLESS STEEL CORP.) 29 August 2019 (2019-08-29)	1-3
P, A	WO 2023/074657 A1 (NIPPON STEEL CORP.) 04 May 2023 (2023-05-04)	1-3

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

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Date of the actual completion of the international search

19 July 2023

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
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Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
WO	2022/075405	A1	14 April 2022	(Family: none)	
WO	2022/075406	A1	14 April 2022	(Family: none)	
JP	2018-35381	A	08 March 2018	(Family: none)	
JP	2019-143228	A	29 August 2019	(Family: none)	
WO	2023/074657	A1	04 May 2023	(Family: none)	

REFERENCES CITED IN THE DESCRIPTION

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- JP 2012136742 A [0005] [0008]